Glass ionomer cements: an investigation into ionic processes within the cement with respect to time

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GLASS IONOMER CEMENTS:

AN INVESTIGATION INTO IONIC PROCESSES WITHIN THE CEMENT WITH RESPECT TO TIME

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Science, University of London.

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Dental Biophysics Unit, Centre for Oral Growth and Development,
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Dedicated to:

My parents

&

Prof J.C. Elliott

ABSTRACT

A series of experiments were performed to understand the ionic processes in glass ionomer cements.

Fluoride release from fluoroaluminosilicate glasses in deionised water and artificial saliva

Inorganic artificial saliva was used to compare the release of fluoride from four fluoro-aluminosilicate glasses (AH2. LG26Sr, LG125 and LG26). The glasses were used in their raw form and as an acid washed glass and pseudocement. Results showed two different trends. AH2 released more fluoride in artificial saliva relative to deionised water and the LG glasses released less in artificial saliva relative to deionised water.

Kinetics of fluoride release from glass ionomer cements: influence of ultrasound and radiant heat

Two conventional GIC's Fuji IX and Ketac Molar were used, along with commercial GIC's Amalgomer, Amalgomer CR and Glass Carbomer which was also radiant heat set. The experimental glass used was LG30 which is a fluoride free glass and was mixed at 7:1 ratio with 2% NaF solution. It was observed that ultrasound increases the release of fluoride whereas radiant heat reduces the release of fluoride.

Investigation into secondary setting mechanism of glass ionomer cement: hydrolytic stability of aluminiosilicate-acetic acid cements

Six glasses were used LG26, LG30, LG117, Anorthite, Na-Anorthite. Glasses were mixed with acetic acid and made into discs. These were matured for 1, 2, 3, 6 and 24 hours then immersed in 40ml of deionised water. After 24hours they were assessed for visual disintegration using a scale developed for this purpose. It was noted that MP4 never formed stable cement; LG26, LG117, Anorthite and Na-anorthite immediately formed a stable cement whereas LG30 formed a stable cement only after 24hours. Inductively Coupled Plasma analysis on the release of ions showed that Al was released in quantities comparable to glass-polyalkenoate cements hence suggesting that acetate cements are actually Al-acetate type cements.

Declaration

I declare that the material in this thesis is entirely my own work and that I have attributed any brief quotations, both at the appropriate point in the text and in the bibliography at the end of this piece of work, to their authors.

I also declare, that I have not used extensive quotations or close paraphrasing and that I have neither copied work from another person, nor used the ideas of another person without proper acknowledgement.

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Foreword

Parts of this thesis have been published in journals and also presented at various conferences. Published papers are included in Appendix A and abstracts for conferences are included in Appendix B at the back of this thesis.

The experiments included in Chapter 2 was presented at PEF 2006 at Dublin.

The experiments on effect of ultrasound on fluoride release have been presented at BSDR 2007 at Durham and PEF 2008 at London. It is also published as a paper *(J MaterSci: Mater Med (2010) 21:581-595).*

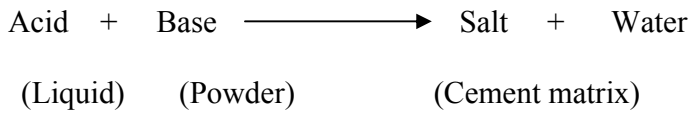
The experiments on acetate cements have been presented at BSDR 2007 Durham and PEF 2009 Glasgow. It also appears as a paper *J MaterSci: Mater Med (2008) 19:541-545.*

Also included in Appendix A is a draft paper which looks at the potential of gassifier slags to develop glass ionomers for use as adhesives in the construction industry.

CHAPTER 1

INTRODUCTION

Dental Cements are a versatile class of materials which find use in a variety of clinical applications such as cosmetic and temporary filling materials; protective cavity liners; luting agents for crowns, bridges, inlays and orthodontic appliances; root canal fillings and pulp cappings. Although a wide range of these cements is available, all of them are essentially 'acid-base reaction cements' formed as a result of an acid-base hardening reaction that occurs when a base like powdered solids are mixed with acidic liquids. This reaction may be represented by the following equation:



The base or the powder, as it is referred as in this context, is either an amphoteric or slightly basic oxide which can be easily decomposed by acids. They may be simple oxides like zinc oxide or complex alumino-silicate glasses.

The acids are aqueous solutions of phosphoric or polycarboxylic acids.

The setting reaction commences as soon as the powder and liquid are mixed. This involves the penetration of hydrogen ions (protons) or H_3O from the liquid into the powder particles liberating metal ions which migrate into the liquid where they combine with the anion to form a salt like gel matrix. As the reaction progresses the

hydrogen bonds in the liquid are replaced by stronger metal ionic bonds giving rise to gelation, setting and hardening. Thus a kind of continuity of structure is maintained throughout the course of the reaction. A higher powder:liquid ratio is used than is required for neutralization of the acid therefore the set cement consists of partly reacted powder particles embedded in the cement matrix which act as reinforcing fillers.

1.1 Types of dental cements:

All the dental cements, with the exception of glass ionomer cements, are based on zinc oxide. These cements are briefly discussed below.

Zinc Phosphate Cement,

Based on zinc oxide powder and aqueous solution of phosphoric acid. It has limited use in modern day dentistry since its acidic nature renders it irritant to the pulp, it is also eroded by acidic oral fluids and is extremely brittle in nature.

.

Zinc polyacrboxylate cement,

Zinc polycarboxylate cements are based on zinc oxide as the base, but use a polycarboxylic acid as the liquid. Invented by Smith (1998), this was the first adhesive dental cement, a property imparted by the polycarboxylic acid. It is commonly used for luting, lining and as a periodontal pack.

Glass Ionomer cement,

Glass Ionomer Cements are the only aesthetic dental cement used in clinical dentistry. The cement is formed by reacting an ion leachable glass powder with a polycarboxylic acid. The cement is currently used for luting, lining and restoration. One formulation (SerenoCem^{TM} , Axis Medical Ltd, UK) is also used as a bone cement. Currently new formulations are also being developed to allow for its use as aluminium free bone cement. Apart from these, it has also been considered as underwater cement for North Sea pipe lines, as a replacement for plaster of Paris in slip casting and as a model material. Properties such as long term fluoride release make the material suitable for use with modern day techniques of Minimal Intervention dentistry and Atraumatic Restorative Dentistry. However there are limitations to the use of this material due to moisture sensitivity during early stages of its setting producing weaker cement. Due to this they need to be protected against early moisture contamination to prevent the cement from weakening. Recently ultrasound has been used to accelerate the setting of glass ionomer cements. This has also led to improving the mechanical properties of glass ionomer cements. Rushe and Towler (2006) have reported an increase in fluoride release from glass ionomers set by ultrasound.

This thesis is structured in such a way that it looks at the kinetics behind the release of fluoride from glass ionomers in deionised water and artificial saliva. It also aims to

understand the kinetics by which ultrasound effects the release of fluoride from these materials.

The final part of the thesis investigates the chemistry behind the maturation of glass ionomer cements. An interesting property of glass ionomer is their tendency to show an increase in mechanical properties with time. These changes have been attributed to the formation of a silica network, but this theory is highly debatable

CHAPTER 2

GLASS IONOMER CEMENTS

It has been almost thirty years since the first Glass-ionomer cements (GIC), now officially termed as 'glass polyalkenoate cements', were introduced into the dental world. In recent years, this material has undergone further development resulting in the availability of a range of materials which undergo setting or 'curing' via different proportions of acid-base and free radical reactions. In the wake of these developments it seems essential to define what actually GICs are. To serve this purpose, the following definition seems an adequate description of the chemistry and properties of the material:

"The term glass-ionomer cement is reserved exclusively for a material consisting of acid-decomposable glass and a water soluble acid that sets by neutralization reaction which takes place within a clinically acceptable time." (McLean, 1994)

Ever since its advent, GIC have received a mixed response from clinicians. It is acknowledged for its chemical adhesion with the tooth and continuing fluoride release (Wilson, 1989; Smith, 1998), but also it is subjected to criticism due to its lack of physical strength and translucency (Crisp *et al.* 1976; Mount and Makinson 1982). Despite this criticism, the material has found its place in a broad spectrum of applications such as luting/lining cement; base, or dentine substitute under composite resin; sealant over an active carious lesion and a restoration in its own right. The driving force in all these aforementioned applications is indeed the chemical adhesion

with tooth and the long term fluoride release (Anusavice, 2003; Mount and Hume, 1998; Mount, 1998).

2.1 Development of Glass-ionomer cements

The inspiration for the development of GIC can be traced back to the era of clinical dentistry which was governed by the use of amalgam, gold and porcelain as restorative materials. The limitations of these materials drove the need for new materials which could be used for luting/lining purposes and which also had a better aesthetic appeal. This paved the way for the development of the zinc phosphate cement by Pierce in 1879, which was later further modified by Ames and Fleck (Ames, 1892; Fleck, 1902) to give the modern day zinc-phosphate cement. Coinciding with Pierce's discovery was Foster's zinc oxide eugenol cement which soon gained popularity due to its obtundant effect on the pulp (Smith, 1998). Despite all these developments, the first breakthrough on the aesthetics front was the silicate cement. Developed originally in 1873 by Thomas Fletcher, the silicate became popular in 1904, only after it had been modified by Steenbock of Berlin. Due to these ongoing developments, the end of the first quarter of the twentieth century saw three basic types of dental cements namely, zinc phosphate cement, zinc oxide eugenol cement and silicate cement. Over the next 50 years these cements underwent considerable technical improvement, but generally the fundamentals of their setting chemistry remained unchanged.

In 1963 the idea of polyelectrolyte cement was developed which involved the reaction of metal oxide with reactive water soluble polymers. Based on this concept Smith produced the first zinc polyacrylate cement using zinc oxide and poly(acrylic acid). By 1964, this cement had been developed into a usable system. It was capable of chemically bonding to the mineral apatite phase of enamel (figure 2.1) by chelating the calcium ions due to the use of poly(acrylic acid). Poly(acrylic acid) also has the ability to form hydrogen bonds with collagen in dentine (Beech, 1972). After undergoing technological improvements and clinical trials the material became commercially available in 1968. In the next decade the material underwent considerable development and materials containing fluorides and using copolymers became commercially available.

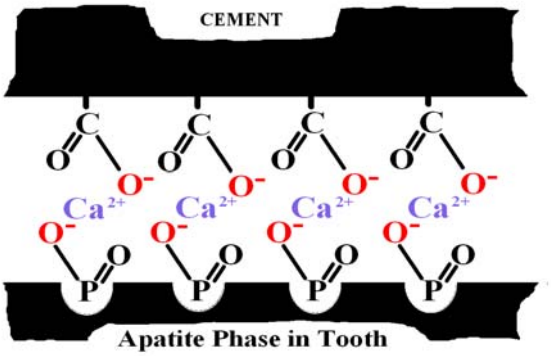


Figure 2.1: Bonding of polyacrylate cements with tooth.

In spite of the novel properties of these polyacrylate cements, the metal oxide component rendered them opaque and hence not aesthetically acceptable. This led to the development of formulations using zinc-containing glass ceramics and silicate cement powders, but these had problems like prolonged setting time when mixed with poly(acrylic acid). Wilson and Kent made a major development in this direction by taking poly(acrylic acid) and mixing it with an ion leachable glass (Wilson and Kent, 1972). The resultant product was given the name aluminosilicate polyacrylate (ASPA) or glass-ionomer, which was a hybrid of the dental silicate cement and the carboxylate cement. The development of more reactive glasses with high fluorine content and the discovery of the effect of tartaric acid in improving the setting properties resulted in the first practical Glass Ionomer cement (GIC) in 1972.

These earlier materials however had drawbacks mainly related to their sluggish setting. They showed prolonged sensitivity to moisture and when set they were rather opaque. However, since these early materials appeared various modifications have been carried out which have led to materials with better characteristics. These modifications included:

(i) Use of alternative polymers such as acrylic/maleic acid as the poly acid component (Nicholson, 1998);

(ii) The use of vacuum dried polymer powders blended with the glass and activated by the addition of water (Prosser *et al.,* 1984)*;*

(iii) The development of cermet containing cements in which the filler consists of a cermet which is silver sintered to the surface of calcium fluoroaluminosilicate glass. These materials have their use in situations where radiopacity is required and for core buildup under crowns (McLean and Gasser, 1985);

(iv) Metal reinforced cements in which a metal such as silver tin alloy or stainless steel is added as an inert filler to conventional glass ionomer in an attempt to reinforce the set cement (Simon, 1983; Williams *et al.*, 1992);

(v) Resin-modified cements in which the conventional acid-base reaction of GIC are complemented by photochemical polymerization of added monomers and initiators.

2.2 Glass Ionomer as a "non-dental" Cement:

Glass Ionomers received considerable attention during early 1990s as cements in other branches of medicine. Excellent biocompatibility was reported (Sasanaluckit *et al.* 1994) and in one study Meyer *et al.* (1993) argued that although aluminium had found its way into the cells there was no evidence of cytotoxicity possibly due to the formation of non-toxic complexes with silica. Clinical trials reported good results for use in procedures like alveolar ridge build up (Duvenage *et al.* 1993), reconstruction following removal of bone tumours (Lindeque *et al.* 1993), fixation of cochlear

implants (Ramsden *et al.* 1992) and craniofacial reconstruction surgery (Zollner *et al*. 1994). However, these materials received a major setback when they were withdrawn from clinical use in France in 1994 (Renard *et al.* 1994). This was following severe post-operative problems with two patients who underwent translabrynthic otoneosurgery and bone reconstruction with glass ionomer cements. Extremely high levels of aluminium were observed in the lumbar cerebrospinal fluid, serum and urine. Since the case report of this incident is poorly written it is unclear if this event may have occurred due to operator error in the surgical technique. Following this series of events researchers have produced several formulations of aluminium free glasses for use in glass ionomers for such purposes. These glasses either use zinc (Boyd and Towler, 2005) or iron (Harrel-Gullingham *et al*. 2006) to replace aluminium.

2.3 Components of Glass-ionomer Cements

Conventional Glass Ionomer cements have the following constituents:

- ***Glass powder:*** A specially formulated acid-degradable fluroaluminosilicate glass.
- ***Acid:*** The acid is a homopolymer of acrylic acid or a related copolymer. (+)Tartaric acid is added to improve the working and sharpen the setting time
- ***Water:*** The reaction medium

2.3.1 Composition and nature of the glass component:

The glasses used in GIC are fluoro-alumino-silicates. These are different from conventional glasses which are mainly soda lime silica glasses. These glasses possess a highly crosslinked O-Si-O linkages and are chemically stable in nature and do not react with conventional acids. Such glasses would serve no purpose in GIC since in order to produce set cement it is essential that the glass is reactive in nature and capable of releasing metal cations. However, the addition of network modifying cations to these glasses disrupts the O-Si-O linkages to produce non bridging oxygens. The resulting glass then represents an ionic polymer where the negative charge on the network (produced by non-bridging oxygen) is balanced by the positive charge of the cation. For glasses used in GIC, alumina acts as the intermediate oxide i.e it can take part in glass structure but cannot form glass on its own. The addition of alumina produces negative sites such as the AlO_4^- tetrahedra making these glasses "acid decomposable" hence allowing them to be used in cement formation. Fluoro-alumino-silicates are produced by the fusion of silica, alumina, calcium fluoride and calcium oxide with aluminium fluoride, aluminium phosphate and cryolite (Na_3AlF_6) added in minor quantities. Structurally, these glasses are based on AlO_4 and SiO_4 tetrahedra with a three dimensional glass structure (Figure 2.2). O is at the vertex and Si and Al are at the centre of the tetrahedron.

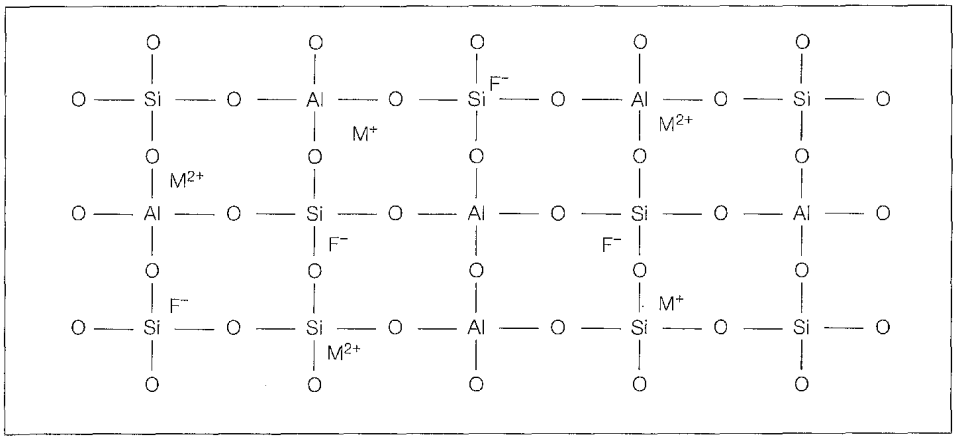


Figure 2.2: Skeletal structure of fluoroaluminosilicate glass (a tetrahedron) (Davidson and Mjör, 1999). [Note: the structure is 3-D but is drawn in 2-D for simplicity]

Alkaline ions or alkaline earth ions like Na^{+}, Ca^{2+}, and Sr^{2+}, exist near the Al^{3+} ion in order to charge balance AlO_4^{-} tetrahedra. These modifying ions can also result in the formation of non-bridging oxygen. It was originally believed that fluoride and phosphate ions included in the glass structure do not form a part of the skeletal structure of the silicate network (Davidson and Mjör, 1999) however some studies have shown the existence of phosphate as a network former (Dupree *et al*. 1989; Kirkpatrick and Brow 1995) and there is strong evidence that PO_4^{+} tetrahedron locally charge balance AlO_4^{-} tetrahedron.

The glasses are commercially prepared by fusing the mixture of its ingredients (Table 2.2) at 1200°C to 1550°C. In the next step, the melt glass is shock cooled resulting in the formation of coarse granules (frit) which are then ground by dry milling in a ball mill to produce a particle size depending upon its application. Generally, a particle

size of <50μm is preferred for restorative cements whereas a <20μm is produced for the luting type of material (Wilson and McLean 1988). In either case, ball milling is often followed by acid-washing of the glasses with 5% aqueous acetic acid. This is done in order to reduce the reactivity of the glass (Schmitt *et al.* 1983)

Table 2.2: Components of fluoroaluminosilicate glass and their effects (compiled from Mount and Hume, 1998; Wilson and McLean, 1988)

Component	Percentage	Effects
SiO_2	29.0	These are three essential components of the glass which fuse to form the Calcium fluoroaluminosilicate glass. Glasses higher in SiO_2 (more than 40%) are more translucent whereas those high in CaF_2 or Al_2O_3 are more opaque.
Al_2O_3	16.6	
CaF_2	34.2	
Na_3AlF_6	5.0	Complements the fluxing action of CaF_2 i.e. reduce fusion temperature.
$AlPO_4$	9.9	Improves translucency and adds body to the cement paste.
Sr, Ba, La, Salts	-------	Used to replace calcium fully or partially to give radiopacity to the glass.

Early work on simple glasses suggests that the Al_2O_3/SiO_2 ratio is crucial in determining the glass reactivity (Wilson *et al.* 1980; Kent *et al*. 1979) however more recently Griffin and Hill (1999) have provided evidence that this ratio has no significant influence on the properties of glass ionomer cements derived from fluor-alumino-phospho-silicate glasses.

Fluoride fluxes (CaF_2 and Na_3AlF_6) apart from lowering the fusion temperature of the glass, impart the unique property of fluoride release from the cement. Griffin and Hill (2000) reported that the glass transition temperature, Tg, for glasses prepared in their experiments fall by approximately 200 ^oC when the amount of fluorine is increased. They explained that the reduction in the temperature is caused by the replacement of bridging oxygens (BOs) by fluorines to form non-bridging fluorines in the glass. Thus, it disrupts the network and allows the relaxation phenomena to take place at lower temperature. In addition fluorine converts Ca^{2+} to F-Ca(n) complexes reducing the number of non-bridging oxygens (NBOs) attached to Si. The presence of fluorine in the glass structure also affects the rheological and setting properties of glass ionomer cements. A fluorine containing glass will be more "network disrupted" and hence more susceptible to acid attack. Crisp and Wilson (1974) found that increasing the fluoride content aids in the extraction of ions from the glass. De Barra and Hill (2000) also found that increasing the content of fluorine in a glass reduces the working and setting times of the cement.

According to ISO recommendations, calcium is wholly or partially replaced by strontium, barium or lanthanum to impart radiopacity to the set cement. Strontium seems to be an ideal candidate since it has a similar ionic radius to that of calcium and hence can replace it without disrupting the glass and producing any loss of translucency (Debb and Nicholson, 1999).

2.3.1.1 Types of Glass Systems

Three main systems have been described by Hill and Wilson having different firing temperatures (Hill and Wilson, 1988):

Type I: $SiO_2 – Al_2O_3 – CaO$ (1350 - 1500 ^oC)

Type II: $SiO_2 – Al_2O_3 – CaF_2$ (1150 - 1300 ^oC)

Type III: $SiO_2 – Al_2O_3 – CaO – CaF_2$ (1250 – 1500 ^oC)

$SiO_2 – Al_2O_3 – CaO$ Glasses:

Only glasses containing less than 61% silica (by weight) can form cements (Hill and Wilson, 1988). In powdered form the majority yield fast setting cements that set between 2 and 10 minutes. The compositional region for more slowly setting glasses is very restricted. Glasses in the anorthite region ($CaO.Al_2O_3.2SiO_2$) have compressive strengths that are lower than those in the gehlenite region ($CaO.Al_2O_3.SiO_2$). Broadly speaking, strength is inversely proportional to the silica content. There is an approximate relationship between strength and setting time. The optimum strength is achieved with setting times between 2minutes 45 seconds and 3 minutes and drops off either side (Hill and Wilson, 1988).

$SiO_2 – Al_2O_3 – CaF_2$

Glasses used in dental glass ionomers are of this type to which cryolite ($Na_3Al_2F_6$) is often added as a flux and also aluminium phosphate. Some glasses are transparent

e.g. if alumina and CaF_2 are approximately equal by mass and there is >35% silica. These are shock cooled and if reheated they phase separate.

SiO_2 is an acidic oxide and Al_2O_3 is an amphoteric oxide. Their ratios control the acid-base balance of the glass. As the ratio falls below 1.33 the setting time increases slightly. It was originally suggested that if the SiO_2/Al_2O_3 ratio is less than 1.33 then phase seperation of fluorite and corundum take place and the glasses become opaque (Hill and Wilson, 1988). However it was later found out that the presence of corundum is more likely to be a result of incomplete melting of the glass.

Increasing the SiO_2/Al_2O_3 ratio decrease compressive strength until it reaches zero. Increasing the ratio above 1.3 leads to the setting time being increased rapidly until at 3.0 the glasses cease to form cements (Hill and Wilson, 1988).

The repleacement of CaO with CaF_2 would be expected to make the glass less basic and less reactive. The change in the glass structure may well affect the basicity of the glass for the following reason. F^- has a similar ionic radius to O^{2-}. The replacement of O^{2-} by the F^- reduces the screening of the central cation therefore strengthening the cation-oxygen bond. This would be expected to make the glass less susceptible to acid attack. However, he F^- ion is non bridging and therefore breaks the structure offsetting this effect.

$SiO_2 - Al_2O_3 - CaO - CaF_2$

These glasses are hybrids of the two previous types. They have unusual features and various discontinuities. All glasses are clear except for the high fluoride glasses at the end of the range, which contains crystals of fluorite (CaF_2). There are two discontinuities encountered when the CaF_2/CaO ratio is altered. There is little change in the working and setting times of the cement when the CaF_2/CaO ratio is changed from 0 to 1:5. At a ratio of 1:3, the glass becomes extremely reactive and mixing it with a polyacid solution generates considerable heat and a solid mass is formed before mixing is complete. Further increases in the CaF_2/CaO ratio beyond 3:1 yield glasses with similar behaviour. .

Phase Separated Glasses:

Most GICs were thought to be phase separated. Currently, whether this is the case or not is a matter of some conjecture (Griffin and Hill, 1999). Phase separated glasses yield stronger cements both in flexure and compression compared to clear glasses. As with all glasses, working time can be extended by washing the glass with dilute acetic acid (Schmitt *et al*., 1983). In the case of phase separated glasses, this procedure removes the Ca^{2+} from the surface of the phase separated droplets and hence reduces the calcium extracted at the start of the reaction. The consequence of washing the glasses removes the surface cations that are extracted at the start of the reaction thus slowing the rate of set. The release of Ca^{2+} and Al^{3+} ions from phase separated

glasses have been observed to proceed at different rates and that one phase is leached selectively.

All glasses, once having been fired are normally acid washed to reduce their reactivity. This preferentially depletes ions used in setting. The original work was carried out by the company ESPE (Seefelt, Uberbey, Germany).

2.3.2 Composition and nature of the acid component:

Acids used in the conventional glass ionomer system are polyelectrolytes. These, as the name denotes, are both polymers and electrolytes and hence are soluble in water. Polyelectrolytes used in GIC are the poly(alkenoics). These polyacids include the homopolymers and copolymers of unsaturated mono-, di-, and tri- carboxylic acids. Of these, the most important used to date have been poly(acrylic acid)s, copolymers of acrylic and itaconic acids (Crisp *et al.* 1980) and copolymers of acrylic and maleic acids (Schmit *et al.* 1981). The polyacids are generally prepared by free radical polymerisation of the appropriate monomers in aqueous solution in the presence of a chain transfer agent and an initiator such as ammonium persulphate. These polyacids consists of linear chains with no cross linking but have pendant acid groups (Wilson and McLean, 1988). To produce a cement of adequate mechanical properties it is essential that the polyacids used have a molecular weight in the range of 40,000 and 60,000, the higher the molecular weight the better will be the mechanical properties,

however in practice molecular weight is limited by viscosity, and some balance has to be achieved between concentration, viscosity and molecular weight (Wilson *et al.* 1989).

The polyacid used in the original glass ionomer was 50% by weight aqueous solution of poly(acrylic acid) (Crisp *et al.* 1975). However, poly(acrylic acid) molecules being flexible and mobile are capable of intermolecular hydrogen bonding. This results in gelation of poly(acrylic acid) solutions on storage prepared at a concentration greater than 45% by weight. It was found that methylation of the poly(acrylic acid) inhibits the gelation process(Crisp *et al.* 1975) however cements prepared from such a liquid stained in the mouth. Crisp and Wilson (1977) hypothesised that the copolymers of acrylic acid with other saturated carboxylic acids would be less susceptible to gelation due to reduced stereoregularity. Based on this assumption they synthesized a copolymer of acrylic and itaconic acid which proved to be indefinitely stable to gelation at a concentration of 50% m/m. Due to greater number of carboxylic acid groups, cements produced from copolymers with higher acid functionality, were found to be harder than those of poly(acrylic acid) (Mount and Makinson, 1982). However, it was also observed that cements based on acrylic acid copolymers show less adhesion with tooth structure (Aboush and Jenkins, 1986) and are less resistant to acid attack (Setchel *et al,* 1985; Wilson *et al.* 1986) than cements of poly(acrylic acid).

(+) Tartaric acid is an important additive in the glass ionomer system. It is added at a level of 5% or 10% in order to improve the handling properties, which it does by extending the working time and sharpening the setting time (Crisp *et al.* 1975). The release of ions from the glass into the matrix is facilitated by tartaric acid which reacts preferentially with the glass readily forming complexes with these ions and preventing early binding of cations to the poly acid chains (Crisp and Wilson, 1974; Barry *et al.* 1979; Prosser *et al.* 1982). By Using FTIR analysis, (Nicholson *et al.* 1988) suggest that this is because (+) tartaric acid delays the formation of calcium carboxylate. Raman analysis also confirms this finding (Young *et al*. 2000). An increase in compressive strength has also been reported with the use of tartaric acid (Crisp *et al.* 1975).

2.3.3 Water: the reaction medium

Glass-ionomer cements are water based materials and hence water plays an important role in their setting and structure. It serves as a solvent and a medium for transporting the ions. Apart from this water also hydrates the siliceous hydrogel and the metal poly(acrylate) salts formed (Wilson and Mclean, 1988).

Water is present in the set cement in at least two different states depending on whether they can be removed or not by desiccation over a suitable desiccant. These states have been classified as ‘evaporable’ and ‘non-evaporable’ or more commonly

referred to as 'loosely bound' and 'tightly bound' water respectively (Wilson *et al*. 1979). Loss of loosely bound water during initial setting stages retards the setting and produces surface crazing and cracks; whereas moisture contamination at this stage results in loss of soluble ions producing weak cements (Wilson *et al*. 1979; Causton, 1981). As the cement matures, the ratio of tightly bound water to loosely bound water increases decreasing its susceptibility to desiccation accompanied by an increase in strength and modulus and a decrease in plasticity (Paddon and Wilson, 1976; Wilson *et al*. 1981).

2.4 Chemistry of the Setting reaction

The setting reaction is an acid base reaction with the ion leachable glass acting as base and the acid being poly(acrylic acid) or its copolymer (Crisp and Wilson 1974). The setting process is in three overlapping stages (Crisp and Wilson, 1974)

Stage 1: The decomposition of the glass powder

Stage 2: Gelation-precipitation of cations and anions

Stage 3: Maturation phase.

2.4.1 Decomposition of the glass powder

This phase may be best described as the ion leaching or extraction phase. During this stage ionisation of the carboxylic acid liberates protons (H^+) from the carboxyl

(COOH) group. These protons attack the surface of the glass liberating Al^{3+}, Ca^{2+}, Na^{+}, F^{-} (if present) and $H_2PO^{-}_4$ ions into the aqueous phase (Wilson and Proser, 1982). Barry and co workers (1979) found that this attack was not uniform but seemed to take place more at calcium rich sites in the glass since these areas are more basic. Whatever the nature of attack, it results in the formation of silicic acid which later condenses to form silica gel (Wasson and Nicholson 1990, 1991; Wilson and Nicholson 1993). Crisp and Wilson (1973) predicted that as a result of this attack 20-30% of the glass particles are degraded, however Billington *et al.* (2006) argue that approximately 7% of the glass is consumed to produce the cement matrix. This degradation of the glass surface and cross linking of polyacids is accompanied by a rise in pH (Crisp and Wilson 1973) and the viscosity of the cement paste (Wilson and Mclean, 1988).

2.4.2 Gelation Phase

As the reaction continues, ions released from the glass accumulate and are removed by precipitation as insoluble polyacrylates. Al^{3+}, Ca^{2+}, F^{-} forming metallic salt bridges with free (COO^{-}) groups resulting in the cross linking of polycarboxylate chains and ultimately leading to setting. This process continues until all the ions are insoluble. It is important to note that not all -COOH groups loose their hydrogen ions to form COO^{-} ions. This is because when most of the carboxylic groups have ionised, the negative charge on the polymer chain increases. This results in the positively

charged ions becoming more strongly bound to the polymer chains hence making it difficult for the metal ions to replace them. Furthermore, as the density of the cross links increases, it hinders the movement of metal ions towards carboxyl sites. Due to these reasons the neutralization reaction does not quite go to completion.

It has been shown that calcium polyacrylate is largely responsible for the initial gelation and setting of the cement in phase separated glasses producing a clinically hard material within 4-10 minutes of mixing. This is followed by a slower formation of aluminium salts which may take up to 48 hours for completion (Crisp *et al*. 1974; Barry *et al*. 1979). However, FTIR analysis has shown that finally both salts are present in equal quantities.

The fluoride and phosphate ions form insoluble salts and complexes. Na^+ contributes to the formation of orthosilicic acid on the surface of the glass particles which converts to silica gel as the pH rises. The silica gel assists in binding the powder to the matrix (Mount and Hume, 1998).

2.4.3 Maturation Phase

Soon after the gelation phase the material undergoes what is commonly known as the "maturation phase". During this stage the material has been shown to increase in compressive strength. According to Wilson and Prosser (1982) this is due to the less

mobile aluminium cross-linking the remaining -COOH acids or by replacing the already crosslinked calcium ions. More recently, Pires and co-workers (2004) have pointed at the maturation related release of the more covalently bound "network forming" aluminium ions to complement the cross-linking phenomenon. Interestingly, Boyd and Towler (2005) have observed a maturation phenomenon in a GIC formulated from aluminium free calcium-zinc-silicate glasses. Since the glass did not contain any 'less mobile' aluminium ions, it suggests the existence of other mechanisms to be associated with improve in mechanical properties as a result of maturation phenomenon.

Wasson and Nicholson (1990) using Inductively Couples Plasma (ICP) found that silica is released in large amounts during the decomposition of the glass and hypothesised its role in cement formation. Such a release has also been observed by Demayer *et al.* (2002) using FTIR analysis. Wasson and Nicholson (1993) demonstrated the role of silica in the maturation process and associated it with the increase in compressive strength of the cements. Although, a possible candidate, the authors did not look at the presence of factors other than silica. Using IR and NMR analysis Matsuya *et al.* (1996) have also related the increase in compressive strength with the silica phase in the matrix but they too ignored the presence of any complimentary mechanisms.

Apart from the above factors, hydration has also been associated with the maturation phenomenon. Wilson *et al.* (1979) found an increase in the ratio of bound to un-bound water with maturation and have correlated it with the increase in compressive strength. The presence of free and bound water has also been observed in silica desiccants. Since, the post hardened silica network formed in GIC has been found to be similar to that of amorphous silica (Matsuya *et al.* 1996) it may give a possible explanation for this phenomenon of free and bound water in GIC.

CHAPTER 3

FLUORIDE RELEASE FROM FLUORO-ALUMINO-SILICATE GLASSES IN WATER AND ARTIFICIAL SALIVA

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3.1 Introduction

Clinical dentistry cannot deny the caries preventive effect of fluoride (ten Cate, 2004), but what remains a controversy is the mode of uptake of fluoride (Thevadas *et al.* 1996; Hellwig and Lennon, 2004). For many decades it was thought that fluoride has to be ingested to produce its anticariogenic effect and this effect was considered to be due to the incorporation of the fluoride into the apatite crystals during tooth eruption. However, it is a known fact now, that the caries-preventive effect of the fluoride is almost entirely posteruptive (Hellwig and Lennon, 2004; Fejerskov *et al.,* 1996). This mode of action has been described by researchers as "fluoride inhibits demineralization and enhances remineralization" (ten Cate, 2004).

The remineralization effect of the fluoride is due to the fact that fluoride ion is readily exchanged for the hydroxyl ion of the hydroxyapatite resulting in the formation of the fluoroapatite. Fluoroapatite cannot be dissolved by acids having a pH above 4.5 (Guida *et al.* 2002;Thevadas *et al.* 1996; Jenkins, 1999).

During the remineralization cycle, the demineralization effect of the acids is reversed if the pH is neutral and there are sufficient Ca^{2+} and PO_4^{3-} ions in the oral environment to enable rebuilding of the partly dissolved apatite crystals. This process is greatly enhanced by the presence of fluoride ions at the reaction site (ten

Cate 2004). However, whilst the anti caries effects of fluoride are well documented, the exact amount of fluoride required to give this effect has not been established.

3.2 Fluoride release from Glass Ionomer Cements:

Glass Ionomer cements are known to release clinically beneficial amounts of fluoride (Guida *et al,.* 2002; Khouw-Liu *et al.,* 1999; Jones *et al.,* 2003). The irony, however, is that leachable fluoride had not been intentionally included to make the cement suitable for dental use, but it occurred as a constituent of the several chemicals used in the manufacture of the glass (Williams *et al.,* 2002).

3.2.1 Source of fluoride

It is not clear as to how and from where the fluoride ion arrives at the surface of the cement. However, it is hypothesized that all intrinsic fluoride must initially come from the glass (Williams *et al.,* 2002). Fluoride in the glass is released into the matrix during the setting reaction (Palmer *et al.,* 2004). An important point to note here is that the fluoride released from the cement along with sodium and perhaps calcium ions in order to maintain the electrical neutrality of the cement, and due to this dependency on other ions the amount of fluoride released from the cement cannot be determined solely by the quantity of fluoride in the initial glass (Thevadas *et al.,* 1996).

3.2.2 Mechanism of fluoride release

During the setting of GIC, the fluoride ions arise initially from the surface of the glass particles which are then held in the siliceous gel of the matrix. Since fluoride ions do not form part of the cement matrix, thus a continuous exchange of fluoride can occur from the cement depending on the gradient of fluoride in the oral environment at any given time. However, the mechanism behind the release of fluoride from glass ionomer cements has not been understood completely, but all researchers seem to agree on the kinetics associated with the fluoride release according to which at least two processes are occurring simultaneously i.e. a short term fluoride burst release and a long term fluoride release. This can be demonstrated by the equation below which adequately and accurately describes the cumulative fluoride $[F]_c$ release from a restorative glass ionomer in distilled water (De Moor *et al.* 1998).

$$[F]_c = \frac{([F]_I\, t)}{t + t_{1/2}} + \beta\sqrt{t}$$

$[F]_I$= Maximum value of fluoride released during short term reaction; **t**= time; **$t_{1/2}$**= 'half-life' of short term release i.e. the time required for the fluoride released by short term reaction to reach half of its maximum value; **β**= a constant which is a measure for the driving force of the long term release.

A large amount of the fluoride released from GICs is during the "short-term release" phase which occurs within a few days of placement in the oral cavity. This amount then declines sharply during the first week and stabilizes after 2-3 months. The long

term release of fluoride is substantially lower, but it appears to be sufficient to prevent caries (Mount and Hume 1998).

The process of diffusion seems to be associated with the long term release of fluoride from glass ionomers. This is evident by Forsten's (1990) study which showed the existence of a linear relationship between the amounts of fluoride released and the square root of time, thus following the theory of simple diffusion. In another study Williams *et al.,* (1999) also pointed toward a relationship between the surface area and the amount of fluoride released, which again shows the existence of a diffusion mechanism. However an erosive mechanism also seems to complement the fluoride release since studies have shown an increase in fluoride release in an acidic environment (Thevadas *et al.,* 1996).

3.2.3 Factors effecting fluoride release

Fluoride release has shown to be dependent upon variables such as the composition of the glass and polyalkenoic acid, the relative proportions of the constituents in the cement mix, the mixing process and the elution medium (De Witte *et al.,* 2000).

The relationship between the composition of aluminosilicate glasses and its effect on fluoride release can be observed from Williams *et al.* (2002) study where a sodium free glass LG26 released lower fluoride than a sodium containing glass G338. This

may be attributed to the high solubility of sodium. However, in glasses where calcium is substituted with strontium for the purpose of radiopacity, a substantial increase in fluoride has not been observed. The only slight increase by strontium has been attributed to its increase density which affects the powder/liquid mixing ratio (Guida *et al.*, 2002).

Hill *et al.* (1995) suggest that the dominant fluoride release is by an ion exchange mechanism whereby fluoride ions are exchanged for hydroxyl ions in water rather than by counter ion mechanism involving release of an alkali metal ion. The ion exchange mechanism for fluoride release explains the reduction in pH of acidic solutions (Nicholson *et al.* 1999)

The amount of fluoride release in different elution media is an interesting phenomenon to observe since the oral cavity provides an environment of varying pH and ionic concentration. Various researchers also reported an increase in fluoride release in an acidic environment, due to surface degradation (De Moor *et. al* 1998; Czarnecka *et al.* 2002). This increase in fluoride release at a lower pH enhances the anticariogenic properties of GIC since the caries process also decreases the pH of the environment surrounding tooth. Furthermore their study also showed the release of more fluoride in an acidic environment. This increase in fluoride release was also previously observed by De Moor *et al.* (1998). Hadley *et al.* (2000 and 2001) have also observed the phenomenon of surface degradation on exposure of glass-ionomer

cements to neutral NaF solution. Since the solution used in this case was a neutral one, the presence of ions in the elution medium may be a possible explanation for the surface roughness.

Amongst the various elution media used for fluoride release artificial saliva is an important one since it provides a close simulation of the oral environment. Mallakh and Sarkar (1990) found that glass ionomers released more fluoride in deionised water than in artificial saliva. This pattern of fluoride release was also observed by Williams *et al*. (1997 and 2001) using the same artificial saliva. Although the mechanism behind the reduction has not been understood but it has been proposed to be either due to the higher ionic strength of the artificial saliva or probably the calcium in the artificial saliva forms an insoluble calcium fluoride layer on the surface of the cement (Williams *et. al* 2001).

The findings of Williams *et al.* (1997 and 2001) and Mallakh and Sarkar highlights the difference in fluoride release in artificial saliva compared with that in deionised water. This not only questions the clinical correlation of studies in deionised water, but it also suggests that further work is required in this area in order to understand the pattern of fluoride release in the oral environment.

3.3 Aims and objectives of the experiment

The main aim of this experiment is to compare the fluoride release from four different glasses in deionised water and artificial saliva. The glasses used are of a different composition so as to evaluate the effect of different elements on the fluoride release.

The second aim is to evaluate, in deionised water and artificial saliva, the pattern of fluoride release at different cement forming stages.

The third aim is to compare the free and complex fluoride release in deionised water with that in artificial saliva.

3.4 Materials and Methods

3.4.1 Materials

3.4.1.1 Glasses

Four formula glasses were selected for use in the experiment. These were the AH2, LG26, LG26SR and LG125. The composition of these glasses is shown in Table 3.1.

Table 3.1: Composition of fluroaluminosilicate glasses (weight percentage).

Glasses	**Oxides**								
	SiO_2	Al_2O_3	CaO	SrO	P_2O_5	CaF_2	SrF_2	NaF	AlF_3
AH2	39.52	23.60	0.0	0.00	3.62	13.65	0.0	9.91	9.70
LG26	24.3	27.5	15.1	0.0	19.1	14.0	0.0	0.0	0.0
LG26SR	20.0	22.6	0.0	23.0	15.8	0.0	18.6	0.0	0.0
LG125	21.5	24.3	0.0	24.7	16.9	12.4	0.0	0.0	0.0

AH2 has a unique composition due to the presence of Sodium in it. The LG26 replaces Sodium with Calcium, whereas in LG26SR calcium is substituted with strontium. LG125 contains a mixture of both Calcium and Strontium.

The particle size of all the glasses was assessed using Malvern particle size measurement machine (Section 3.2.1). It was found, by virtue of the particle sizer, that all the glasses had a similar particle size except for LG26. This glass was thus ball milled for 30 hours and then sieved using a <20 micron sieve. The glass was then re-assessed for particle size.

3.4.1.2 Acid washed Glasses

All the four glasses were acid washed. For this purpose, 20 gram of each glass was placed in a plastic container with 67ml of deionised water and 10ml of 35% acetic acid (BDH Laboratory). The mixture was stirred for 24 hours with an electro-magnetic stirrer. After 24 hours the slurry was filtered through the filter paper and the residue was then first washed with deionised water in order to remove the surface ions and then it was washed with acetone. After the washing, the residue was allowed to dry, for 24 hours, in a fume cabinet. Once dried, the acid washed glass residue was broken up using mortar and pestle and then sieved through a <50 micron sieve.

The particle size of the acid washed glasses was also measured. The results showed all the acid washed glasses having a similar particle size except for LG26. This glass was then mixer milled (Glen Creston Ltd, Type MM 200) for 200mins. After the milling cycle, the particle size of LG26 was again measured. The acid washed glasses were also stored in plastic bottles.

3.4.1.3 Pseudo-cements

The pseudo-cements were prepared for each glass type using the acid washed glass and acetic acid. The powder/liquid ratio used was 4:1, except for AH2 for which it was 3:1. (Note: A different mixing ratio was used for AH2 because it is an very reactive glass and it was difficult to mix it at 4:1 ratio). After mixing, the produce was

packed into circular rubber moulds having a diameter of 1cm and a thickness of 1mm. A glass slab was placed on the surface and finger pressure was applied to the glass slab to allow even distribution of the material. The assembly was then clamped under constant load for 1 hour.

3.4.1.4 Elution media

As per the requirements of the experiment, each of the glasses and pseudo-cements were stored in deionised water and artificial saliva. The artificial saliva used in this instance was based on the formulation (Table 3.2) described by Fusayama *et al.* (1963).

Table 3.2: Composition of artificial saliva (adapted from Fusayama *et al*. 1963)

Constituent	**Amount** ($gm\ L^{-1}$)
Sodium chloride	0.400
Potassium Chloride	0.400
Calcium chloride.H_2O	0.795
Sodium dihydrogen phosphate. H_2O	0.690
Sodium sulphide.$9H_2O$	0.005

The components of the saliva (Table 3.2) were accurately weighed (± 0.002) and then mixed in 1000ml of deionised water. The freshly prepared solution had a pH of 5.5.

3.4.2 Methods

3.4.2.1 Malvern Particle Size Analyzer

Prior to using the analyser, the analyzer bath was properly washed with deionised water to allow the removal of any impurities. Once clean the analyzer bath was filled with deionised water up to the marked level. Sample data was entered as per the onscreen instructions and then after adjusting for background reading a suitable amount of the sample was added in to the analyzer bath. Once the readings settled down, the measurements for the particle size were performed and the data was output via the printer. After use, the analyzer was re-rinsed with deionised water.

3.4.2.2 Sample Preparation

Samples were produced from raw glasses, acid washed glasses and pseudo-cements for both deionised water and artificial saliva.

Raw glasses

0.12 – 0.14g of the glass was carefully weighed and transferred into the 15ml PE centrifuge test tube. In this way, six samples were prepared and the test tubes were filled with 10ml of deionised water. These samples were shaken and then immediately stored horizontally at 37^{o}C. Six blank solutions of the deionised water used to prepare the samples were also stored with the samples. This was done in order to calculate the background fluoride reading.

Samples for artificial saliva were also prepared in a similar manner and stored in the same conditions. Blank solutions of artificial saliva were also stored with the samples.

At 1, 3, 7, 14, 21 and 28 days of immersion into the elution media, the samples were centrifuged at 4000rpm for 40 minutes after which 8ml of the clear solution from the top was poured of into another test tube. This solution was used to evaluate the fluoride released. The solution remaining in the test tube was discarded and 10 ml of fresh solution was added to the sample. The samples were shaken again and returned to the oven with a new set of blank solutions. This exercise was performed for samples in both deionised water and artificial saliva.

Acid washed glasses

A protocol, similar to the one used for raw glasses, was used for the preparation of samples of acid washed glasses.

Pseudo-cements

Six samples of pseudo-cements were prepared for each glass type using the acid washed glasses. The method used has been described in section 3.1.3. After one hour of their preparation, each pseudo-cement sample was weighed and then ground using mortar and pestle. This ground mass was then put into the plastic centrifuge tube and then 10ml of the solution (either deionised water or artificial saliva) was poured into

the tube. The tubes were then shaken and placed in the oven at 37^{o}C with the respective blank solutions. The solutions were changed using the same procedure and pattern as the one used for raw glasses and acid washed glasses.

3.4.2.3 Measurement of fluoride release

Analysis of the fluoride released was performed using fluoride selective electrode. The electrode used was a Thermo- Orion Ionplus, Model 96-09. Prior to use, the tip of the electrode was flushed with deionised water. The electrode was then filled with the electrode filling solution (Optimum Result A 900061, Thermo Orion). The electrode was then calibrated using fluoride standards prepared in either deionised water or artificial saliva depending on the solution to be measured. Fluoride concentration in the standard was recorded as RmV and then a calibration curve was produced which was used to calculate the fluoride released. The method used to prepare standards in artificial saliva was slightly different than the one used for deionised water.

Standards for deionised water were prepared by serial dilution of 0.1M aqueous sodium fluoride solution (Orion Sodium Fluoride Standard) to give concentrations of 0.001mM, 0.01mM, 0.1mM, 1.0mM and 10mM.

Standards for artificial saliva were produced by serial dilution of 0.1M aqueous sodium fluoride solution in artificial saliva. The concentrations produced were

0.001mM, 0.01mM, 0.1mM and 1.0mM. 10mM standard was not prepared because using it did not produce a good linear plot for the calibration curve. This was probably due to a cloudy precipitate which formed in the 10mM solution. To over come the problem associated with the missing standard, artificial saliva removed from the AH2 glass samples (acid washed and pseudo-cements only) was diluted with three times the volume of artificial saliva in order to bring the fluoride concentration within the 0.1mM and 1.0mM mark. Fluoride analysis for AH2 was then performed on these diluted solutions. The value obtained was then corrected for dilution to obtain the original concentration. The saliva standards were prepared on the day of the measurement since storing them reduced the level of fluoride concentration.

3.4.2.4 Method of fluoride measurement

Fluoride was measured as free fluoride and then with TISAB IV to de-complex the fluoride ions.

Free fluoride measurement

The free fluoride was measured using the following method:

1. For calibration for deionised water, 1ml of deionised water was mixed with 1ml of standard solution on the magnetic stirrer. The fluoride electrode was then dipped into the mix and the reading was recorded from the benchtop display once it reached stability. The calibration was done in ascending order.

For artificial saliva a similar calibration procedure was used except that the standards used were those prepared in artificial saliva and that 1ml of artificial saliva was mixed with 1ml of standard solution.

2. For measurement of samples in deionised water, 1ml of deionised water was mixed with 1ml of sample solution on the magnetic stirrer. The stable reading was then recorded.

   For samples in artificial saliva 1ml of artificial saliva was mixed with 1ml of sample solution and the stable reading was recorded.

   The blanks of both the solution were also tested for fluoride and then this value was corrected for from the samples.

Measurement of total fluoride (TISAB method)

Since the electrode is unable to measure the total fluoride ions, TISAB IV solution was used to decomplex them. This solution was prepared in the following manner:

To 500ml of deionised water in 1000ml volumetric flask add 86ml of concentrated HCl (36-38%), 242g of TRIS(hydroxymethyl) aminomethane and 230g of Sodium L-tartrate dihydrate. The mixture was stir to dissolve and then diluted up to the mark.

The method used for fluoride measurement with TISAB was similar to the free fluoride method except for the following changes:

1. The respective standards were mixed with 1ml of TISAB IV on the magnetic stirrer.

2. The sample solutions for both artificial saliva and deionised water were mixed with TISAB IV on the magnetic stirrer.

3.5 Results

3.5.1 Results for particle size analysis

The particle size analysis was performed as described in section 3.2.1. The results obtained for this analysis are shown in Table 3.3. From the table it can be noted that the particle size for all the glasses is almost equal with not much variation. For all the glasses the particles size seems to reduce after acid-washing except for LG26SR and LG125 which showed a slight increase.

Although AH2 contains sodium the sodium content is low (5.42 weight%) and does not result in any significant solubility at neutral pH.

Table 3.3: Results for particle size analysis.

Glasses	**Particle size (µm)**					
	Raw			Acid washed		
	D 90	D10	D50	D 90	D10	D50
AH2	16.78	1.16	4.13	14.38	1.11	3.57
LG26	16.29	0.71	4.09	13.68	0.58	4.01
LG26SR	13.64	0.52	3.31	13.87	0.57	3.44
LG125	13.85	0.54	3.42	14.29	0.59	3.44

3.5.2 Experimental data

In view of the main aim of this experiment, that is to compare the fluoride release in deionised water with the release in artificial saliva, the data has been organized in a way so as to compare the cumulative fluoride release from 24 hours to 28 days. Statistical analysis has been performed using Student's t-test.

Table 3.4 shows the mean cumulative fluoride release from the raw glasses, acid washed glasses and pseudo-cements. This data is graphically represented in figures 3.1, 3.2 and 3.3.

Table 3.4: 28 days mean (*n=6*) cumulative fluoride release.

Raw Glasses	28 days Mean Cumulative Fluoride release (mg/g glass)			
	Free Fluoride (water)	**Complex Fluoride (water)**	**Free Fluoride (saliva)**	**Complex Fluoride (saliva)**
AH2	6.1 ± 0.0	7.9 ± 0.1	8.4 ± 0.2	13.4 ± 0.3
LG26SR	2.2 ± 0.0	2.3 ± 0.0	1.1 ± 0.1	1.1 ± 0.0
LG125	2.0 ± 0.1	2.0 ± 0.1	1.4 ± 0.0	1.3 ± 0.0
LG26	1.9 ± 0.2	1.9 ± 0.2	2.1 ± 0.0	2.1 ± 0.1
Acid washed glasses				
	Free Fluoride (water)	**Complex Fluoride (water)**	**Free Fluoride (saliva)**	**Complex Fluoride (saliva)**
AH2	8.1 ± 0.1	19.5 ± 0.4	7.8 ± 0.3	15.6 ± 0.5
LG26SR	2.2 ± 0.0	2.3 ± 0.0	1.3 ± 0.1	1.2 ± 0.1
LG125	2.0 ± 0.0	2.0 ± 0.0	1.4 ± 0.1	1.3 ± 0.0
LG26	5.2 ± 0.1	5.4 ± 0.1	2.2 ± 0.0	1.8 ± 0.0
Pseudo-cements				
	Free Fluoride (water)	**Complex Fluoride (water)**	**Free Fluoride (saliva)**	**Complex Fluoride (saliva)**
AH2	9.2 ± 0.2	45.4 ± 0.5	9.5 ± 0.1	79.8 ± 0.4
LG26Sr	4.8 ± 0.3	4.8 ± 0.2	1.2 ± 0.1	1.3 ± 0.0
LG125	3.3 ± 0.2	3.3 ± 0.2	1.1 ± 0.1	1.3 ± 0.0
LG26	4.4 ± 0.2	8.0 ± 0.3	2.3 ± 0.1	2.6 ± 0.1

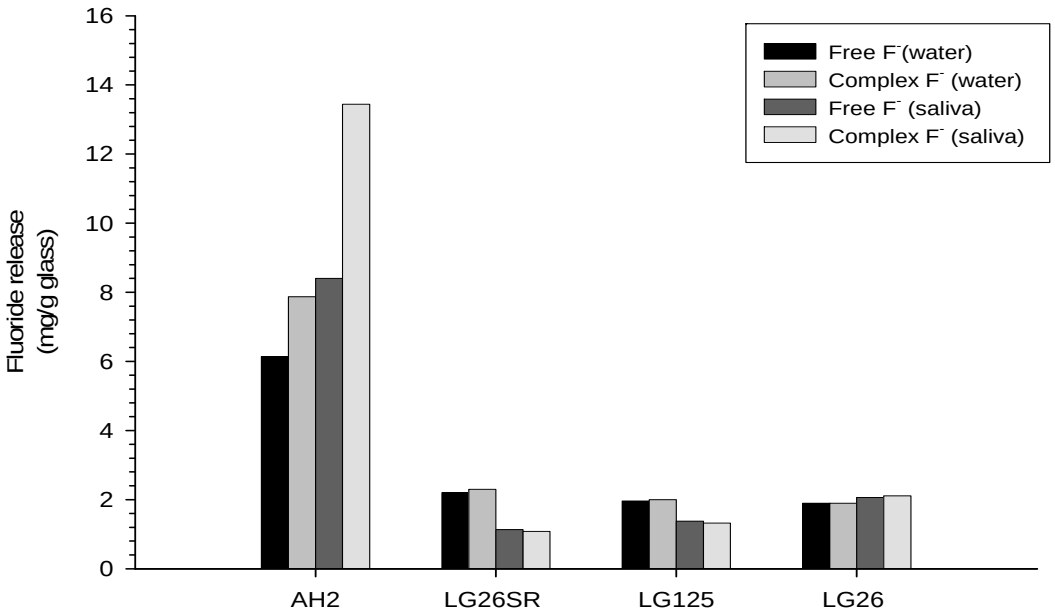


Figure 3.1: Comparison of 28 days mean (*n*=6) cumulative fluoride release from raw glasses in deionised water and artificial saliva.

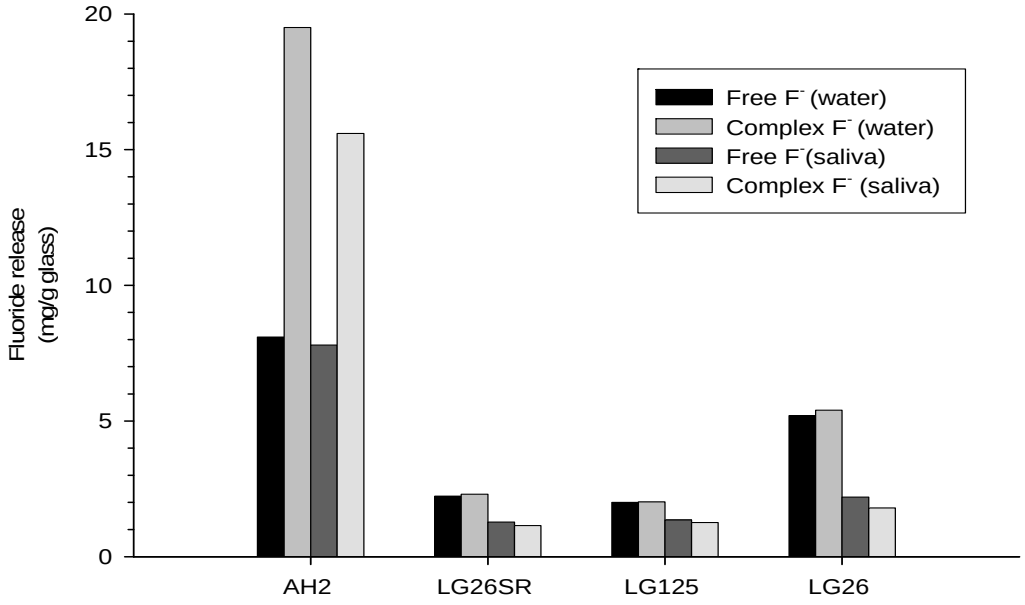


Figure 3.2: Comparison of 28 days mean (*n*=*6*) cumulative fluoride release from acid washed glasses in deionised water and artificial saliva.

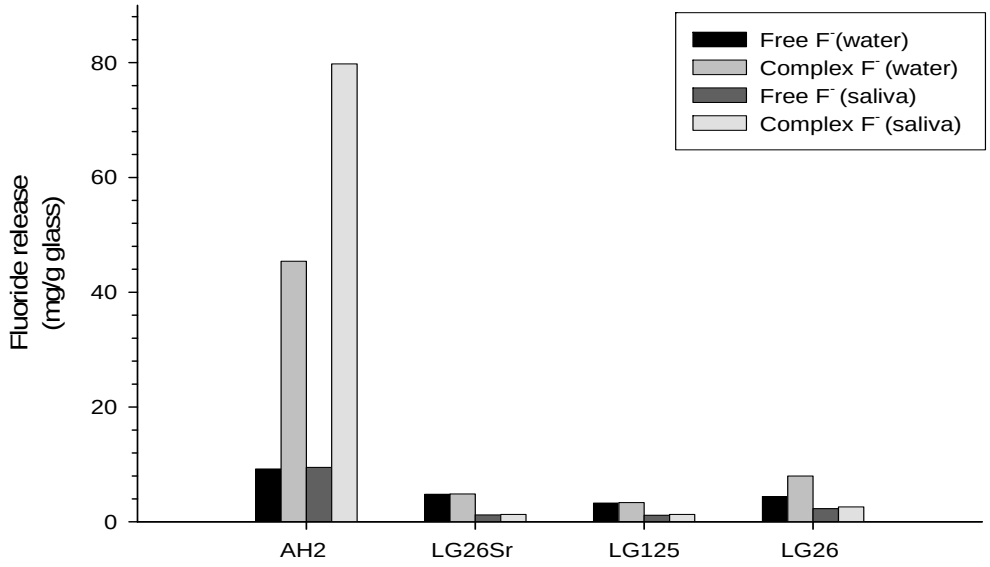


Figure 3.3: Comparison of 28 days mean (*n=6*) cumulative fluoride release from pseudo-cements in deionised water and artificial saliva.

Table 3.5: Comparison of slopes and R^2 values for fluoride with relation to time $^{1/2}$

Glasses	Deionised Water				Saliva			
	Free Fluoride		Complex Fluoride		Free Fluoride		Complex Fluoride	
	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
AH2 (raw)	0.86	0.96	1.08	0.95	1.23	0.96	1.65	0.96
AH2 (acid washed)	1.41	0.99	2.73	0.97	1.40	0.99	1.95	0.96
AH2 (pseudocement)	1.96	0.99	4.47	0.95	1.80	0.99	3.01	0.91
LG26SR (raw)	0.30	0.99	0.31	0.98	0.17	0.98	0.18	0.97
LG26SR (acid washed)	0.37	0.97	0.37	0.95	0.21	0.98	0.17	0.98
LG26SR (pseudocement)	1.04	0.93	1.05	0.94	0.22	0.96	0.20	0.95
LG125 (raw)	0.28	0.99	0.30	0.98	0.23	0.98	0.22	0.99
LG125 (acid washed)	0.34	0.96	0.33	0.95	0.22	0.97	0.20	0.98
LG125 (pseudocement)	0.74	0.99	0.75	0.99	0.20	0.95	0.18	0.95
LG26 (raw)	0.29	0.97	0.27	0.96	0.37	0.99	0.39	1.00
LG26 (acid washed)	1.04	0.98	1.02	0.99	0.38	0.99	0.37	0.97
LG26 (pseudocement)	0.99	0.98	1.23	0.99	0.45	0.97	0.42	0.96

3.5.2.1 Fluoride release from AH2

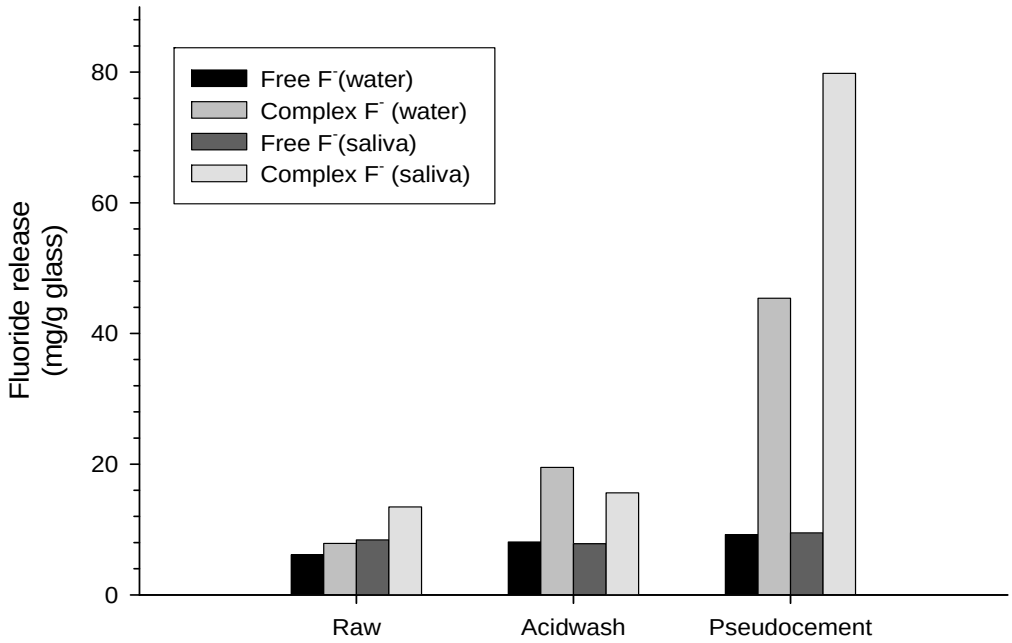


Figure 3.4: Comparison of 28 days mean (*n=6*) cumulative fluoride release from AH2 series in deionised water and artificial saliva.

Fluoride release from AH2 series was the highest (Table 3.4; Figure 3.1, 3.2, 3.3). Amongst the AH2 series, it was observed that the raw glasses released the lowest amount of fluoride in both the elution media, followed by acid washed glasses and then the pseudocements with the highest fluoride release (Figure 3.4). Comparing the fluoride release in deionised water with that in artificial saliva a significant increase in free and complex fluoride was observed for the raw glass (*p=0.001*) where as the pseudocement showed a significant increase in complex fluoride only (*p=0.001*) (Table 3.6). The fluoride release from the acid-washed glass relative to deionised

water was significantly lower (*p=0.002*) when comparing complex fluoride but the decrease in free fluoride was not significant (*p=0.394*) (Table 3.6).

Table 3.6: Effect of artificial saliva on free and complex fluoride release from AH2.

Glasses	Effect of artificial saliva on fluoride release relative to deionised water	
	Free Fluoride	**Complex Fluoride**
AH2*(Raw)*	+37%	+70%
AH2*(Acidwashed)*	- 3%	- 20%
AH2*(Pseudocement)*	+3%	+76%

A significant difference was noted between free and complex fluoride (*p=<0.001*) for each elution media. This difference was lowest for raw glass, followed by acidwashed glass and then pseudocement (Table 3.7).

Table 3.7: Complex fluoride as a percentage of total fluoride.

Glasses	Deionised water	Artificial Saliva
AH2*(Raw)*	23%	37%
AH2*(Acidwashed)*	58%	50%
AH2*(Pseudocement)*	80%	88%

The fluoride release with respect to time $^{1/2}$ was linear in deionised water and artificial saliva (Table 3.5; Figure 3.5). Except for acid-washed glass, the slopes were noted to be steeper in the artificial saliva than in deionised water.

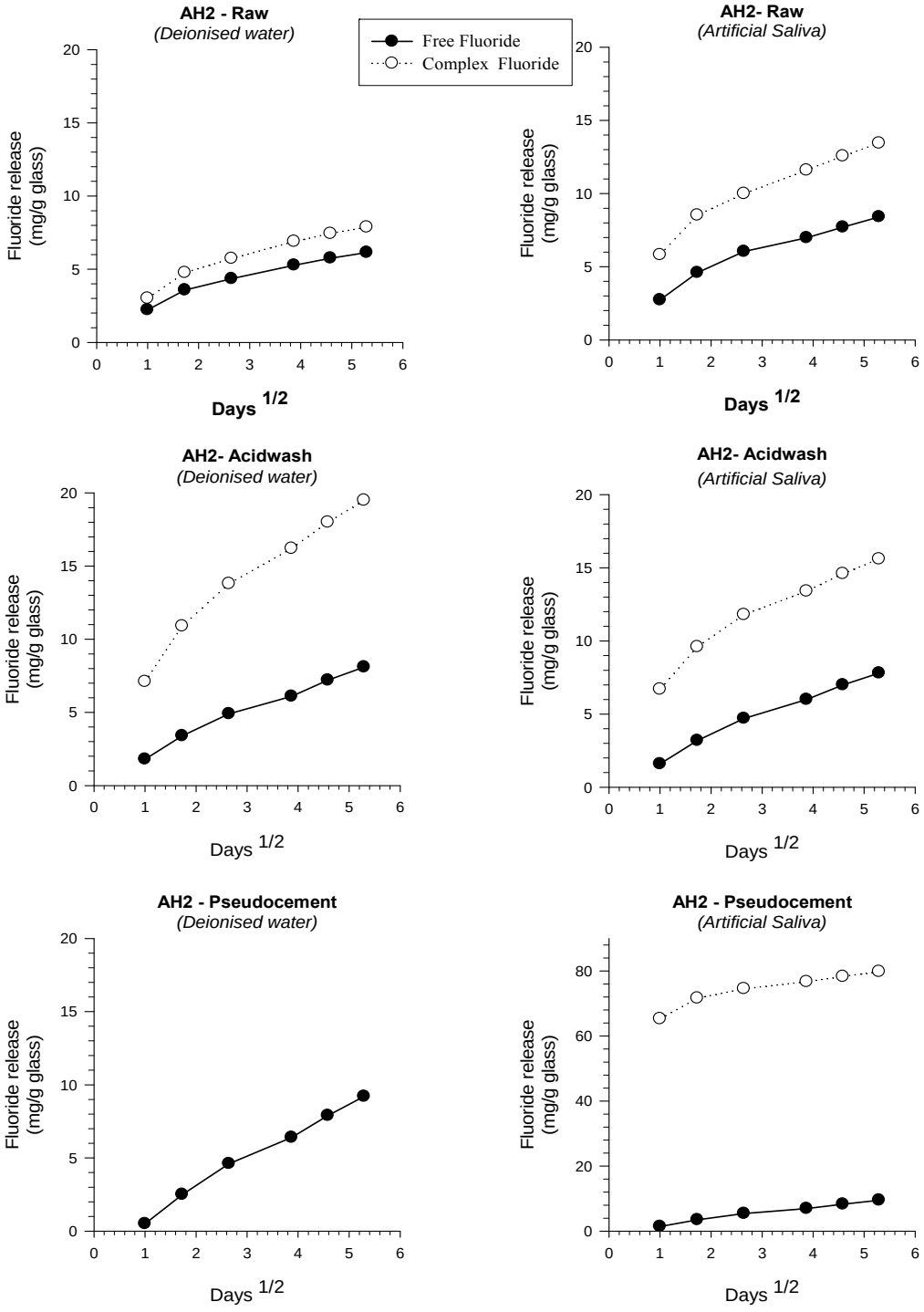


Figure 3.5: Relationship of fluoride release with time^{½} for AH2 series in deionised water and artificial saliva.

3.5.2.2 Fluoride release from LG Series (LG26Sr, LG125 and LG26)

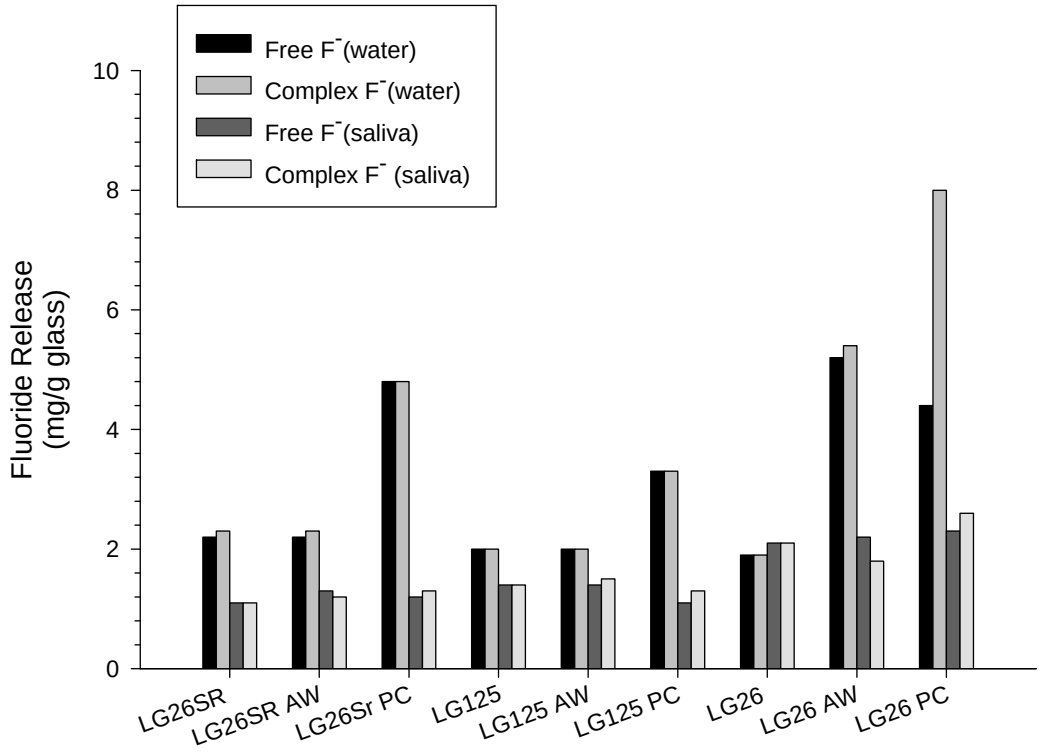


Figure 3.6: Comparison of 28 days mean (*n=6*) cumulative fluoride release from LG series in deionised water and artificial saliva (AW=acid-washed glass; PC=pseudocement)

Relative to deionised water, in the artificial saliva a "damping effect" was noted which significantly decreased the fluoride release from the LG series except for raw LG26 which showed an insignificant increase (Table 3.8).

The highest reduction in fluoride release was observed for the pseudocements with the LG26SR pseudocement showing the most reduction (Table 3.8).

Table 3.8: Effect of artificial saliva on fluoride release of LG series (*HS=highly significant, S=significant, NS = Not significant*)

Glasses	Effect of artificial saliva on fluoride release relative to deionised water		Significance of the change
	Free Fluoride	Complex Fluoride	
LG26SR *(Raw)*	- 52%	- 52%	HS ($p<0.001$)
LG26SR *(Acidwashed)*	- 43%	- 47%	HS ($p<0.001$)
LG26SR *(Pseudocement)*	-72%	-72%	HS ($p<0.001$)
LG125 *(Raw)*	- 35%	- 35%	S ($p=0.002$)
LG125 (*Acidwash)*	- 35%	- 35%	HS($p<0.001$)
LG125 *(Pseudocement)*	- 60%	- 60%	S ($p=0.002$)
LG26 *(Raw)*	+10%	+10%	NS($p=0.156$)
LG26 *(Acidwash*)	- 63	- 66	HS ($p<0.001$)
LG26*(Pseudocement)*	- 47	- 67	HS ($p<0.001$)

A significant difference between free and complex fluoride was observed with acid-washed LG26Sr ($p=0.008$) and LG26 pseudocement ($p=0.003$) in deionised water only.

The LG series showed a linear relationship for fluoride release against time $^{1/2}$ in both the elution media (Table 3.5; Figure 3.7, 3.8, 3.9). The slopes had a lower value in artificial saliva than in deionised water except for raw LG26 which showed a higher value of slope in artificial saliva (Table 3.5).

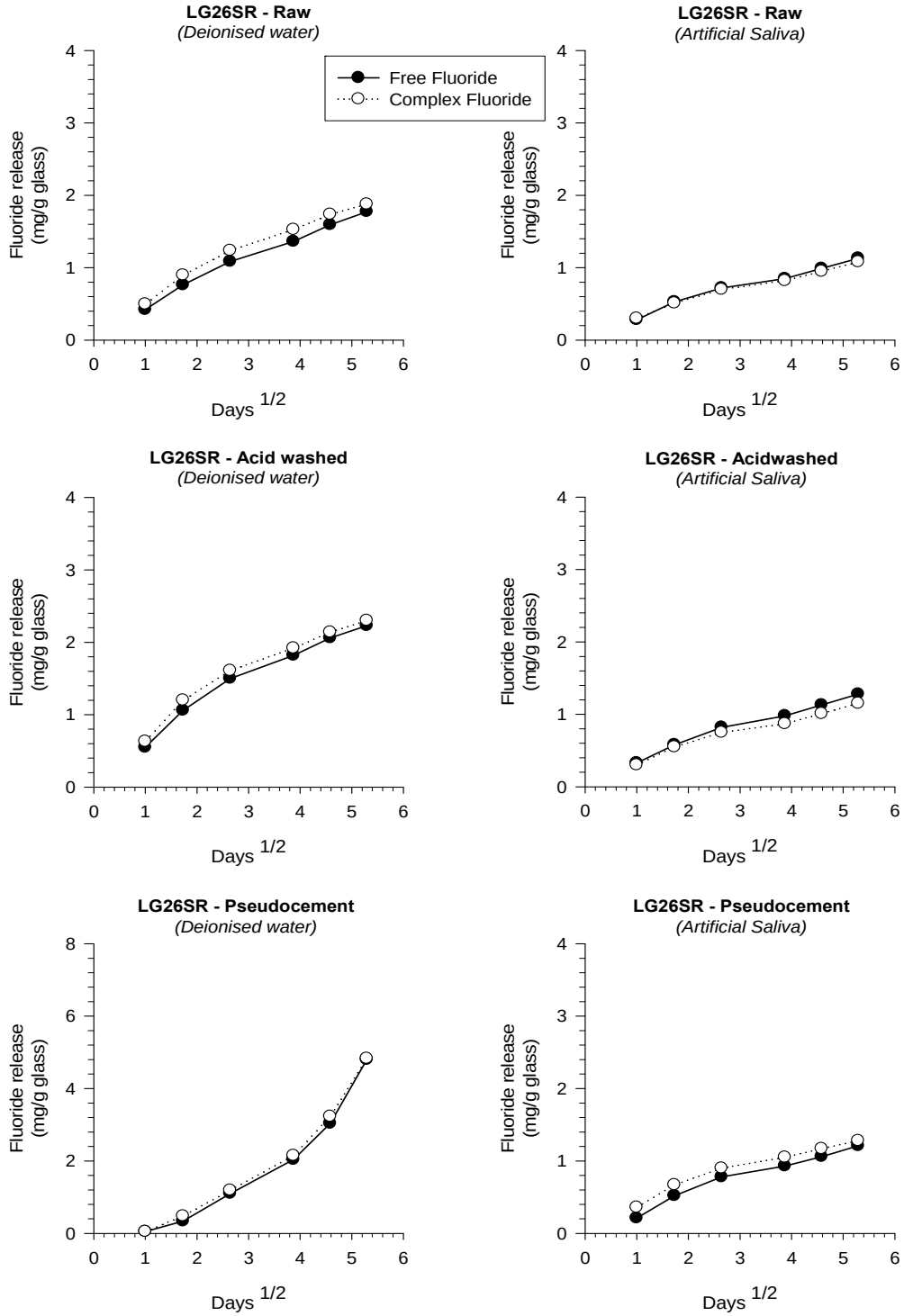


Figure 3.7: Relationship of fluoride release with time^{½} for LG26SR in deionised water and artificial saliva.

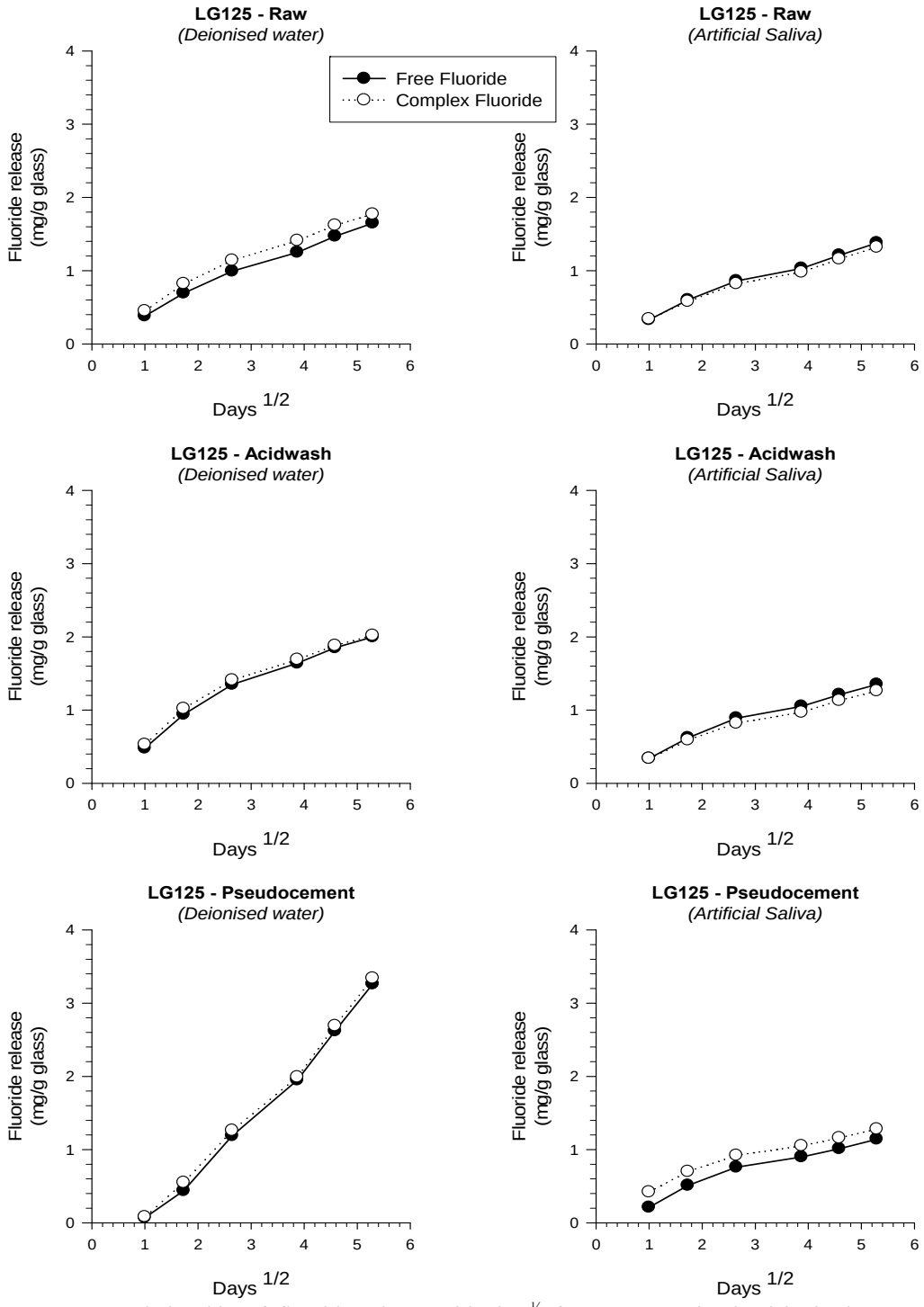


Figure 3.8: Relationship of fluoride release with time^{½} for LG125 series in deionised water and artificial saliva.

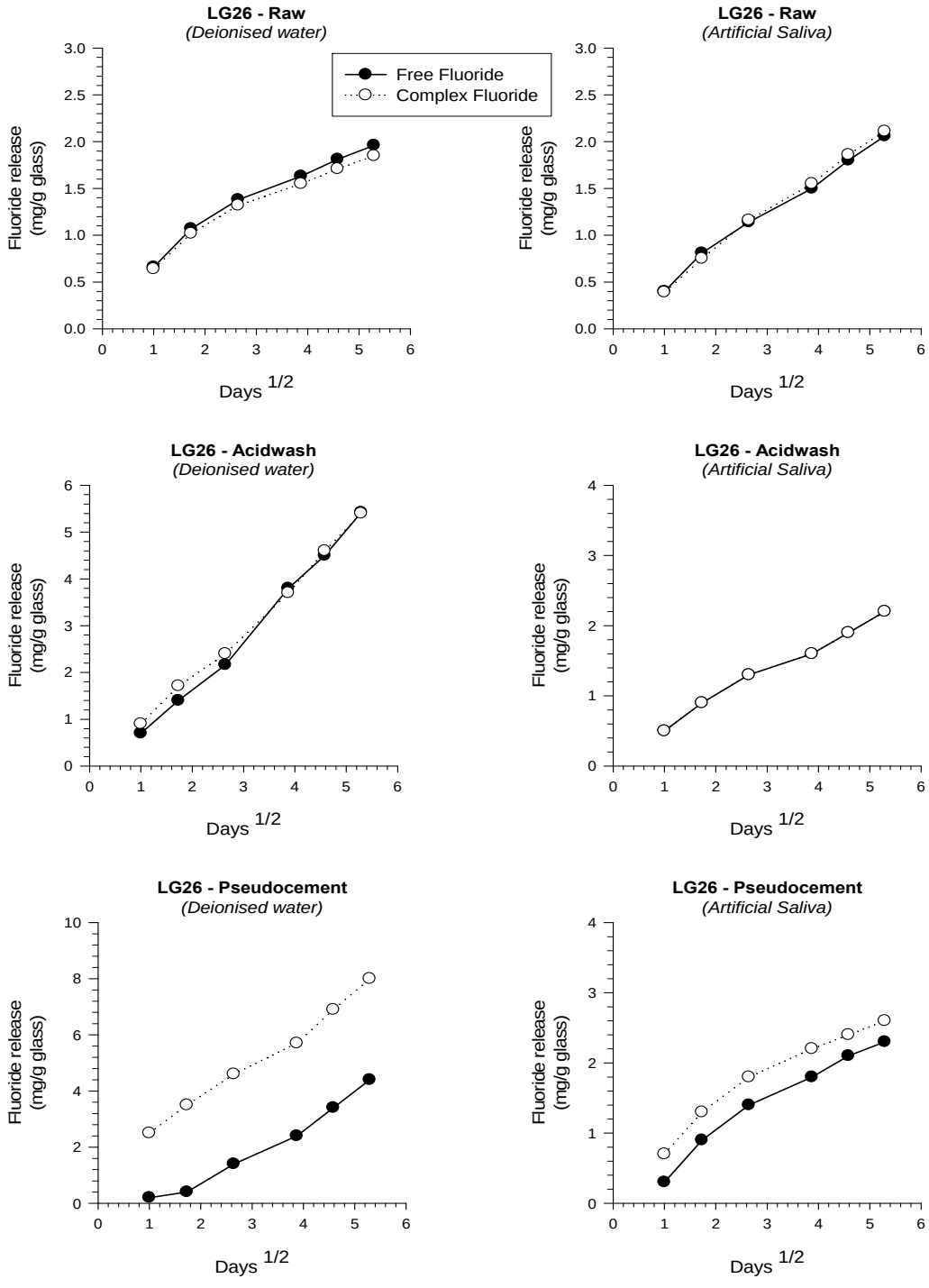


Figure 3.9: Relationship of fluoride release with time^{½} for LG26 series in deionised water and artificial saliva.

3.6 Discussion

3.6.1 Choice of materials and methods

3.6.1.1 Glasses, Acid washed glasses and Pseudo-cements

The glasses used for this experiment were the AH2, LG26, LG26SR and LG125. The AH2 has a similar composition to the commercially used glass G338 whereas the LG series are for academic use. Apart from this, the AH2 is the only glass to contain deliberate sodium. The presence of sodium in the LG series may be regarded as an impurity since it is not an intentional component of their composition. Amongst the LG series, the LG26 contains Calcium and in the LG26Sr the calcium is replaced with strontium. The LG125 contains both strontium and calcium. The reason behind choosing glasses with different compositions was to understand the effect of inherent ions on the release pattern of fluoride in artificial saliva.

Apart from being used in their raw form, the glasses were modified to produce acid-washed glasses and pseudocements.

Acidwashing is a normal industrial process which results in the reduction of reactivity of the glass so as to delay the setting time. The reduction in glass reactivity is due to the removal of surface ions which produces a “depleted glass layer” on the glass surface. The formation of this layer could also influence the release of fluoride from the glass.

The reason behind using pseudocement rather than a real cement was to understand the pattern fluoride release from the cement forming process rather than the cement itself. The acid used to produce the pseudocement in this study was 35% aqueous acetic acid. The use of this acid would help to produce a pseudomatrix and at the same time it would further modify the depleted glass layer around the acid washed glasses. At the same time it allows the cement to be broken up to expose the glass particles.

3.6.1.2 Elution media

The experiment was performed in duplicate, measuring the release of fluoride from the glasses and their modification in deionised water and in artificial saliva. The purpose of using deionised water was to provide a control media for the release of ions. Since the deionised water is virtually free of any ions, it would be interesting to compare the fluoride release pattern in this solution with that in artificial saliva which provides a combination of various anions and cations.

The reason behind using artificial salvia was to emulate the human oral environment as closely as possible so as to study the fluoride release pattern. The artificial saliva used in this study provides pH of the human saliva and also most of the inorganic ions in the human saliva are available in the medium. However the artificial saliva lacks the organic component which is a potential disadvantage. Alternative to this would have been to use artificial saliva with organic components, but since this is a

preliminary study, the use of saliva without organic constituents permits an understanding of the role of inorganic ions in it with the fluoride release pattern. A further option was using real stimulated human saliva, which was considered, but then again the complex and variable composition makes it unsuitable for a preliminary study. A further problem is that human saliva would have easily degraded at 37^{o}C.

3.6.1.3 Fluoride electrode

The Fluoride electrode used in this experiment is Model 96-09 Ionplus Ion selective electrode from ThermoOrion. This type of electrode is easy to use and has the ability to detect the fluoride concentration in a reasonable time with quite good reproducibility. However, it is essential that the electrode is calibrated before use since it carries out comparative measurement against known standards. It is also necessary to monitor the calibration at regular intervals during the measurement session to ensure the uniformity of calibration. The electrode is less effective at measuring very low fluoride concentration where it not only requires a relatively longer time to give a stable reading; but also the calibration plot becomes non-linear. This problem, however, can be overcome by increasing the number of standards for the lower concentration.

For artificial saliva, the non-linearity of the calibration curve was a problem for standard with concentration above 1mM. This presented difficulties in measuring

fluoride release from one glass AH2 which had concentrations above 1mM. However, this was overcome by diluting the samples using artificial saliva by a factor of four prior to measurement. This effectively brought their concentration within the linear part of the calibration curve allowing the fluoride concentration to be measured. The final value was then corrected for the dilution.

Fluoride exists in both free and complexed forms. It is necessary to uncomplex the fluoride ion to carry out fluoride ion measurement. The method adapted here uses the TISAB IV solution (Kakajima *et al.* 1997). The TISAB IV solution (disodium tartrate-tris(hydroxymethyl)methylamine-HCl) forms complexes with ions such as aluminium and thus allows the fluoride to exist in the free state.

There are alternatives to ion electrode measurement of fluoride, an effective and alternative is to use the ICP (Inductively Coupled Plasma). However this technique is not only expensive, but it is not available universally as well.

3.6.1.4 Particle size measurement

Particle size analysis was performed using the Malvern particle size analyzer which provided a quick and easy user interface. The particle size analysis by the system was based on the principle of laser diffraction by the particles. The main problem associated with this technique is that the particle size analysis is based on the

assumption that all particles are spheres. Since most of the particles exist in irregular shapes, they may produce some variation in the values obtained. However all the measurements were carried out in a similar fashion and for comparative purposed this provides a good approach to particle sizes.

3.6.1.5 Experimental methods and associated limitations

An important procedure performed throughout the course of this experiment was to remove and replace the elution media from the test tubes. This method not only allowed the measurement of incremental and cumulative fluoride release, it also provided a low concentration medium for the release of fluoride thus preventing the increasing fluoride concentration in the solution from inhibiting the release as the concentration of fluoride in the solution rises. However the disadvantage associated with this method is that during the change some quantity of the glass particle may be lost, but this amount can be treated as negligible since the centrifuge provided clear separation of the glass from the solution.

Another procedure performed throughout the experiment was the preparation of artificial saliva. Since the mass of the salts in its composition was quite low there was a chance of variation during the weighing process. This was dealt with by increasing the volume of artificial saliva prepared since substantial amounts were required throughout the experiment. This directly increased the mass of the ingredients thus

reducing the degree of variation and providing artificial saliva with similar composition every time.

3.6.2 Factors affecting the experiment

3.6.2.1 Particle Size

As evident from the study of Williams *et al.* (1999) the fluoride release is dependant on the surface area rather than the volume of the glass, therefore it was necessary to match the particle size of the glasses so as to rule out the influence of particle size variability on the comparison of fluoride release in deionised water and artificial saliva. Thus ball mill was used to mill the LG26 glass which had a substantially different particle size than other glasses used. This produced a glass particles distribution which was similar to the other glasses.

3.6.2.2 Mass of glasses used

The mass of glasses used in the experiment varied from 0.12g for the raw and acid washed glasses to 0.20g for the pseudocements. Since a small amount of glasses is used, the fluoride release is at the lower end of the of the electrode sensitivity making it difficult to monitor result variation between samples which otherwise would be evident for high concentration of fluoride release.

3.6.2.3 Phase separation of the glass

Since the glasses used in this experiment contain several components there is a chance of phase separation, especially with AH2, as a result of the manufacturing process. This can provide fluoride rich domains which could influence the fluoride release pattern.

3.6.3 Analysis of the results

3.6.3.1 Linear relationship of fluoride release with time ^{½}

The linear relationship between the fluoride release and square root of time is evident from Table 3.5 with very good correlation. This relationship occurs in both water and artificial saliva. The fluoride release is considered to be driven by the diffusion mechanism (Fick, 1855).

3.6.3.2 Fluoride release from AH2

Relative to the LG series, the AH2 showed the highest fluoride release which may be associated with the high fluoride content of the glass. From figure 3.5 a "burst release" can be observed initially which is more marked in case of the pseudocement similar to the real cement (Forsten, 1990). Such a burst release pattern is associated with sodium containing glasses and has been attributed with the release of fluoride in the form of highly soluble sodium fluoride. However, it was interesting to note that in comparison to deionised water, fluoride release from raw glass and pseudocement

increased when stored in artificial saliva. Considering the fact that glasses used in commercially available GIC have a similar composition to AH2, this finding comes as a contrast with the results of Mallakh and Sarkar (1990) and Williams *et al.* (1997 and 2001) which reported a decreased fluoride release from glass ionomer cements in artificial saliva similar to the one used in this experiment. This may suggest different fluoride release behaviour for fluoro-alumino-silicate glasses and cements.

Although earlier studies have shown that fluoride release from glass ionomer cements increases in an acidic medium due to an erosive mechanism (De Moor *et. al* 1998; Czarnecka *et al.* 2002)., it would be inappropriate to relate the acidic pH of artificial saliva with the increase in fluoride release from AH2 raw glass and pseudocement. This is because the linear relationship between fluoride release and time$^{1/2}$ (Table 6) provides more evidence for the presence of a diffusion controlled fluoride release rather than erosion based one. Furthermore, if the acidic pH of the artificial saliva resulted in the increase in fluoride release, an increase from cements would also have been reported by Mallakh and Sarkar (1990) and Williams *et al.* (1997 and 2001)

Reviewing the AH2 composition (Table 3.1), a possible reason for the increase in fluoride release may be related to its sodium content which disrupts the glass network making it prone to phase separation and hence providing fluoride rich domains. However the decrease in fluoride release from acidwashed AH2 contradicts this phenomenon.

On a comparison of free and complex fluoride in deionised water and artificial saliva, it was noted that a substantial amount of fluoride is released as complexed fluoride in both the media. For the raw glass and pseudocement, there is a considerable increase in complexed fluoride in artificial saliva possibly due to the presence of ions in artificial saliva. However, once again the decrease in complexed fluoride from acid-washed glass contradicts the complex ionic composition of the artificial saliva to be responsible for this. This behaviour of the acid-washed glass in artificial saliva is not clear and requires some further work.

3.6.3.2 Fluoride release from LG26SR, LG125 and LG26

The fluoride release from LG series glasses was substantially lower than the AH2 (Table 3.4) in both deionised water and artificial saliva and the release pattern did not show the burst release. There was little difference in the fluoride release for each elution media from the LG series glasses which suggests that the substitution of calcium with strontium in the glass composition does not have a marked effect on the fluoride release. It appears that the absence of sodium is a more significant contribution to the reduction in fluoride release.

On comparison of the fluoride release in deionised water (Table 3.4) and artificial saliva it was noted that except for raw LG26 there was a substantial decrease in the fluoride release in artificial saliva. This decrease in fluoride release is similar to that observed by Mallakh and Sarkar (1990) and Williams *et al.* (1997 and 2001).

Williams *et al.* (1990) suggest that this reduce may be due to the presence of calcium in the artificial saliva which forms insoluble calcium fluoride. This may account for a distinctive white material clearly distinguishable from the glass after centrifugation of all glasses. However, the role of calcium fluoride in decreasing the fluoride release seems unlikely considering the increase in fluoride release by AH2 and that the raw LG26 release an almost equal amount of fluoride in artificial saliva and deionised water. It seems that since it is essential that there should be a balance in the release of cations and anions from the aluminosilicate glass in order to maintain its electrical neutrality (Nicholson, 1998), the low solubility of calcium and strontium ions in the artificial saliva may have affected the release of fluoride.

Another observation with the LG series was that it showed virtually no difference between free fluoride and complex fluoride in both the elution media. Comparing this with the high difference observed with AH2, it seems that the ions in the artificial saliva are not forming complexes with the fluoride but it is rather due to the inherent ions in AH2 composition which can account for this.

3.6.3.3 Fluoride release from raw glass, acid washed glass and pseudocement

In deionised water it was observed that for all glasses the raw glass released the lowest amount of fluoride, followed by acid washed and then pseudocement. This suggests that the presence of a depleted glass layer enhances the fluoride release from

fluoroaluminosilicate glasses. However, the results of release in artificial saliva show that except for AH2 there was not an obvious difference in the fluoride release from raw glass, acidwashed glass and pseudocement. Although this suggests that the presence of a depleted glass layer does not affect the release, a possible reason behind this is not clear.

3.7 Conclusions

From the experiment two distinct patterns of fluoride release from was observed. This difference seems to be attributed to the difference in composition of these glasses where a sodium containing glass (AH2) showed the highest fluoride release profile with a burst release pattern. On the other hand, the LG series glasses which include calcium and strontium in their composition showed a more gradual release pattern of fluoride in both artificial saliva and deionised water.

Comparing the fluoride release in deionised water with that in artificial saliva, an increase as well as a decrease in the fluoride release was observed, which cannot be explained fully.

CHAPTER 4

KINETICS OF FLUORIDE RELEASE FROM GLASS IONOMER CEMENTS: THE INFLUENCE OF ULTRASOUND, RADIANT HEAT AND GLASS COMPOSITION.

Kinetics of fluoride ion release from dental restorative glass ionomer cements: the influence of ultrasound, radiant heat and glass composition. J Mater Sci Mater Med. 2010 Feb;21(2):589-95.

4.1 Introduction

Early water/saliva contamination leading to a softened or disrupted matrix on the surface of glass ionomer cement is a distinct problem (Davidson and Mjor, 1999). The soft surface adversely affects the properties of the cement when in the mouth. In addition to improvements to the GICs, studies are being carried out into methods accelerating the set to address this problem.

The methods that have been investigated are the application of ultrasound and heat to accelerate the setting (Towler *et al.* 2001; Kleverlaan *et al.* 2004; Algera *et al.* 2005; Brune, 1982). This has been investigated using an ultrasonic scalar device. The results of these studies indicate that application of ultrasound to GICs accelerates the rate of set of these cements. They showed improvements in the physical properties of the GIC. An increased rate of set as indicated by hardness of a GIC Fuji IX (FIX) was observed using a nano-indentation technique (Towler *et al.* 2001). A further study carried out by Kleverlaan *et al.* (2004) showed an increase in the hardness properties and compressive strength of FIX Fast and Ketac Molar (KM) cements. However they stated that for this improvement in the mechanical properties "may partially be explained by the heat effect".

Both studies suggest that the ultrasonic vibration directly enhances the setting reaction of the GIC. The vibration enhances intimate contact of the glass particles

with the polyacid solution thus accelerating the reaction. The compaction of the particles leads to enhanced mechanical properties and has the potential for void reduction. Due to the acceleration of the setting times for GICs, this makes the cements less susceptible to water uptake, therefore reducing the development of a softened matrix on exposure to water.

More recently, Rushe and Towler (2006) demonstrated the influence of ultrasound on the fluoride release of commercial and experimental glass ionomer luting cements.

This study is designed to investigate the effect of ultrasonic setting (UC) on fluoride release from a range of commercial GICs by comparing that from standard set (SC) samples of the same GICs. A further aim of this study is to compare the fluoride release from capsulated and hand mixed version of the same GICs. Additionally the fluoride release of a glass ionomer containing zirconia as a reinforcing and radiopacifying filler will be compared with the product in a zirconia-free version.

The manufacturers of another commercial Glass Carbomer (GC) product advocate the use of the radiant heat (RC) from a commercial dental curing light to produce the accelerated set created by ultrasound and the effects of the two types of radiation on fluoride release will be compared. Ultrasound may influence the fluoride release as a result of changes in the glass polyacid reaction or diffusion rate of fluoride through the cement. To investigate this, a GIC made with a fluoride free glass and with NaF

added to the water component will be studied for the effect of ultrasound on fluoride release rate. Cumulative release will be studied over a period of 28 days to enable both initial ‘‘burst’’ and ‘‘steady state’’ release to be evaluated.

4.2 Materials and Methods

4.2.1 Materials

Four commercial glass ionomers were used in this study. These were Fuji IX Fast (GC Corp), Ketac Molar Aplicap (3M ESPE), Amalgomer and Amalgomer CR (Advanced Healthcare Ltd) and a newly introduced glass ionomer variant Glass Carbomer (Glass Carbomer Products B.V. ,The Netherlands). All these materials were in encapsulated form.

Apart from the above materials model cements were produced using an experimental glass LG30.

The composition of the glasses used is given in Table 4.1

Table 4.1: Composition of glasses used (percentage by weight)

Element	Si	Al	Ca	Na	F	P	Sr	La
FIX	13.7	17.9	0	1.0	10.2	2.2	19.9	0
KM	12.4	15.0	10.1	1.7	13.3	2.0	0	17.6
LG30	14.6	18.1	13.9	0.05	0.04	6.4	<0.01	<0.01
AH2	18.7	15.8	7.1	5.5	12.9	1.6	0	0
GC	20.0	14.1	2.1	1.9	9.0	2.5	13.6	0

GC Fuji IX GP fast (FIX) is composed of a polyalkenoate acid liquid, with glass powder in 0.40/0.11 (g/g) ratio. The powder/ liquid ratio that were used for Ketac

Molar Alicap (KM) capsule were 0.34/0.10 (g/g) ratio. Both the materials have a similar glass composition except for the fact that Fuji IX uses strontium as a radiopacifier and Ketac Molar uses lanthanum

Amalgomer (AM) and Amalgomer CR (AM CR), (ceramic-reinforced) capsules contained the AH2 glass and PAA homopolymer. Amalgomer CR contained 19.7% zirconia particles in the powder component of the capsule.

The Glass Carbomer (GC) is a novel glass ionomer which differs in its composition from other conventional glass ionomers. The composition of Glass Carbomer was obtained by treating a fluorosilicate glass powder with 1)Polydialkysiloxane, where the alkyl group contains 1-4 carbon atoms; 2) An aqueous acid solution. The glass particles are coated with silicone to increase the working and handling time (Van Den Bosch and Van Duinen, [Patent] 2004)

4.2.2 Methods

4.2.2.1 Preparation of Samples

10 specimens of each cement were prepared for each setting process. All sample preparation was carried out at room temperature. After activation the capsule was placed in a rotating mixer, Rotomix for 10 s as per manufacturer's instructions. The mixed capsule was then loaded into the gun. A polyethylene mould of dimensions

3 mm diameter and 2 mm thick was placed on a sheet of acetate and the mixed cement was injected into the mould, then covered with acetate sheet. The acetate sheets were used to obtain a flat surface area of each specimen, therefore ensuring that the dimensions remained the same. The specimens were then left for 6 min to set normally (SC).

A set of 10 ultrasonically set (UC) specimens were prepared and set using ultrasound from a ultrasonic hand piece with a flat tip scaler (EMS Piezon Master 400 Dental Scaler) operating at a maximum frequency of 45 kHz that was set on the maximum power setting. The flat tip of the scaler was moved continuously on the surface in a uniform manner over the acetate sheet where the ultrasonic waves penetrated through into the cement for 55 s as optimized previously (Talal *et al.* 2009). A near uniform US field is found at least to a depth of 4 mm (Harle *et al.* 2002).

For GC a further set of 10 samples was prepared and set using radiant heat (RC) from a commercial dental curing light. Mixed capsules were packed in the mould as described above. A light source which is a blue light lamp with an intensity of 1200 mW was applied to the cement for 90 seconds.

Preparation of Hand Mixed Samples

For Fuji IX, Ketac Molar and Amalgomer, the glass powder and polyacid liquid was extracted from the capsulated forms of the cements. To ensure accurate mixing as per

the P/L ratios given by the manufacturers, the amount of glass powder and liquid used was weighed. The glass and liquid were mixed together on a glass slab. There were 10 SC hand mixed (HM) samples prepared, by mixing for 30 seconds before being placed in a 3mm diameter and 2mm width polyethylene mould. There were a further 10 samples of each material were prepared by employing ultrasound for 55 seconds.

Sample Preparation for LG30

Prior to using LG30 glass it was acid washed (Section 3.4.1.2). The acid washed LG30 was used to produce anhydrous cement 81.3% glass, 17% PAA (50 KDa) and 1.7% tartaric acid (all percentage by weight). The anhydrous cement powder was mixed with deionised water at a powder/ liquid ratio of 7:1 for 40 seconds. The 5 samples were prepared using a 2mm by 3mm cylindrical polyethylene mould and set chemically at room temperature. A further 5 samples where set using US applied for 55 seconds.

Preparation & Setting of LG30 + NaF

The acid washed LG30 is a non fluoride containing glass, therefore it was mixed with 2% NaF solution at a P/L ratio of 7:1 for 40 seconds, after which the cement was placed in a polyethylene mould. Again 5 samples were standard set for 6 minutes at room temperature, and 5 samples were set by applying US for 55 seconds at the highest intensity.

All samples were placed in 15ml centrifugal tubes and left to equilibrate for 24 hours, before adding 10ml of deionised water and storing them in an incubator at 37^{o}C. The deionised water was changed at intervals of 1, 3, 7, 14, 21, and 28 days.

4.2.2.2 Measurement of Fluoride Ions

Fluoride analysis was performed using a Thermo Ionplus electrode. The method for fluoride analysis has been described earlier Section 3.4.2.3

4.3 Results

Results show that US significantly increases the fluoride release from all the materials used (Table 4.3). This increase affects both the initial burst and the long term release which is evident from the increase in values of intercept (c) and slope (m) respectively (Table 4.4). The release of fluoride is also linear to t1/2 (Table 4.3; Figures 4.1-4.5) suggesting that fluoride release is diffusion controlled

Amongst all the materials used UC Amalgomer CR showed the highest release of fluoride (Table 4.2). The lowest, as expected, was from LG30 since it does not contain any “deliberate” fluorine in its composition.

Capsule mixed SC and UC Ketac Molar and Fuji IX showed a relatively higher release of fluoride than its hand mixed counterparts (Table 4.2; Fig 4.2).

For Glass Carbomer, US significantly increased the release of fluoride, however when the material was set using radiant heat, fluoride release was reduced (Table 4.2 and Fig 4.4)

Table 4.2: Cumulative fluoride release from glass ionomer cements (mg F/g cement) (SC=self cure; UC= ultrasonically set; RC=radiant heat cured; HM= hand-mixed; CAPS=Capsule mixed; FIX= Fuji IX, KM=Ketac Molar; AM=Amalgomer; GC= Glass Carbomer)

MATERIAL	Day 1	Day 3	Day 7	Day 14	Day 21	Day 28
SC FIX	0.15	0.25	0.35	0.45	0.55	0.55
UC FIX	0.40	0.70	1.00	1.30	1.50	1.60
SC KM	0.20	0.30	0.40	0.44	0.64	0.74
UC KM	0.40	0.60	0.90	1.02	1.12	1.32
HM UC FIX	0.35	0.53	0.73	0.82	0.92	1.00
HM SC FIX	0.22	0.31	0.39	0.43	0.47	0.50
HM UC KM	0.45	0.62	0.87	0.88	0.97	1.04
HM SC KM	0.14	0.22	0.32	0.35	0.38	0.41
SC HM AM	0.23	0.35	0.52	0.70	0.83	0.92
UC HM AM	0.49	0.85	1.24	1.55	1.83	2.06
SC AM CAPS	0.20	0.28	0.42	0.54	0.65	0.74
UC AM CAPS	0.52	0.95	1.37	1.83	2.16	2.18
SC AM CAPS CR	0.53	0.97	1.14	1.30	1.44	1.45
UC AM CAPS CR	1.07	1.97	2.45	2.88	3.26	3.57
GC UC	0.43	0.72	1.04	1.38	1.64	1.96
GC SC	0.18	0.29	0.42	0.55	0.64	0.76
GC RC	0.18	0.27	0.36	0.46	0.53	0.70
UC LG30 + NaF	0.008	0.013	0.016	0.021	0.025	0.027
SC LG30 + NaF	0.007	0.010	0.013	0.018	0.020	0.021
UC LG30	0.001	0.001	0.002	0.003	0.004	0.004
SC LG30	0.001	0.0011	0.0014	0.0018	0.0018	0.0018

Table 4.3: Effect of US on F release and its statistical significance (Mann-Whitney test) [Relative to SC samples)

Materials	Increase in F release	Statistical significance of the increase
FIX	291%	S *(p=0.015)*
KM	178%	S *(p=0.022)*
HM FIX	200%	S *(p=0.011)*
HM KM	254%	S *(p<0.001)*
HM AM	224%	S*(p=0.022)*
CAP AM	295%	S*(p=0.021)*
CAP AMCR	246%	S*(p=0.006)*
GC	258%	S*(p=0.026)*

Table 4.4: Comparison of linear coefficient, slope and intercept for fluoride release against $t^{1/2}$. (SC=self cure; UC= ultrasonically set; RC=radiant heat cured; HM= hand-mixed; CAPS=Capsule mixed; FIX= Fuji IX, KM=Ketac Molar; AM=Amalgomer; GC= Glass Carbomer)

Material	R^2	Slope (m)	Intercept (c)
FIX SC	0.968	0.0968	0.077
FIX UC	0.982	0.28	0.197
KM SC	0.979	0.12	0.074
KM UC	0.983	0.201	0.258
HM FIX SC	0.9612	0.0495	0.223
HM FIX US	0.9785	0.1261	0.316
HM KM SC	0.9377	0.0456	0.1492
HM KM UC	0.9498	0.1042	0.4742
AM CR SC	0.8904	0.1815	0.5519
AM CR UC	0.9601	0.5093	0.9002
AM SC	0.9987	0.1241	0.0774
AM UC	0.9724	0.3791	0.2851
AM HM SC	0.9893	0.1596	0.0535
AM HM UC	0.9913	0.342	0.239
GC UC	0.9969	0.3451	0.1015
GC SC	0.9977	0.1295	0.0639
GC RC	0.9933	0.1022	0.0363
LG30 UC	0.9915	0.0044	0.0045
LG30 SC	0.9826	0.0034	0.0041
LG30+NaF UC	0.9621	0.0008	7x10-5
LG30+NaF SC	0.8659	0.0003	0.0004

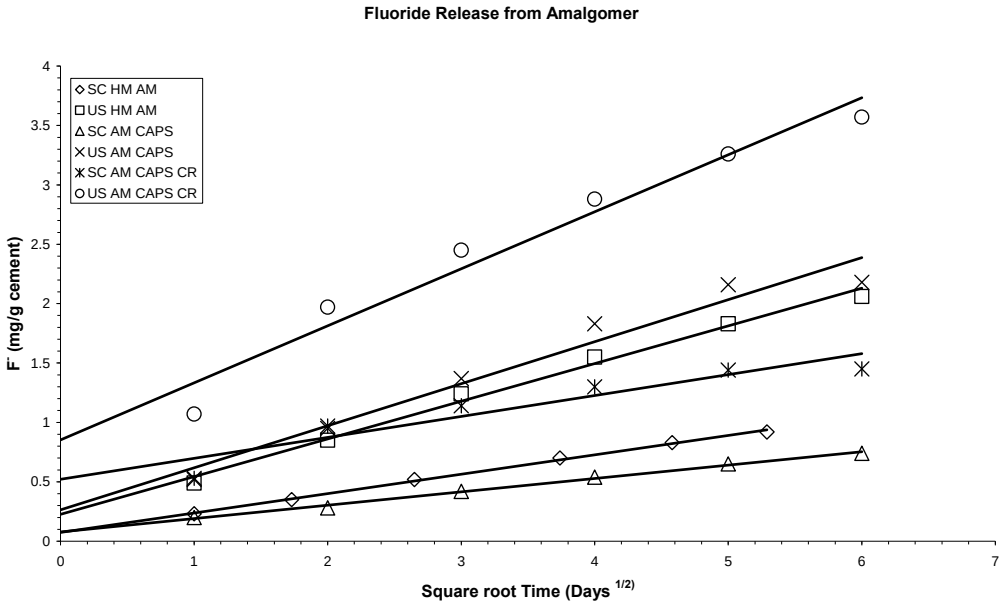


Figure 4.1: Cummulative fluoride release from Amalgomer

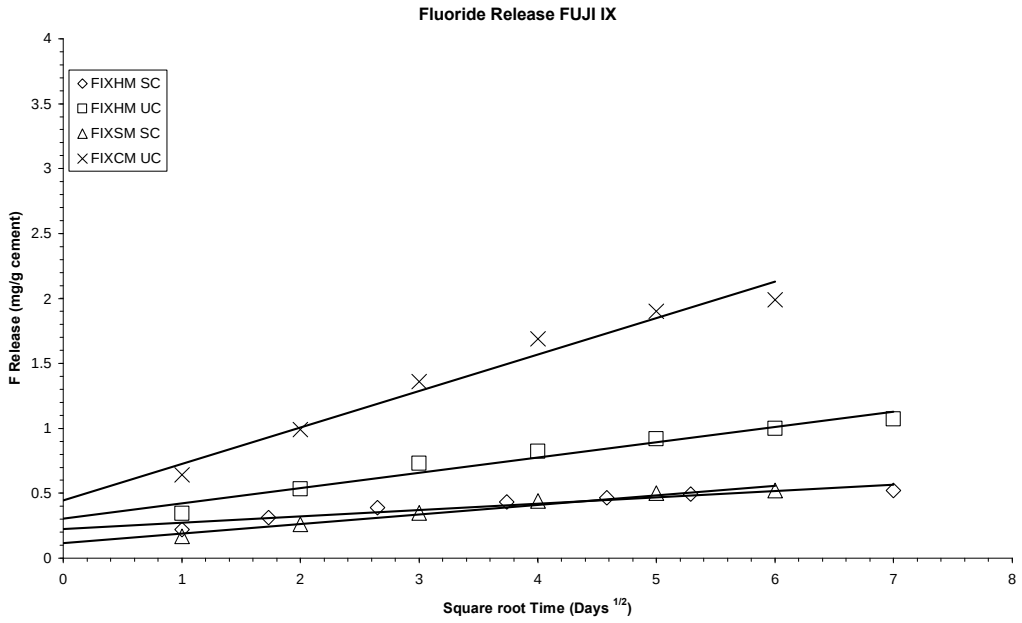


Figure 4.2: Cummulative fluoride release from FUJI IX

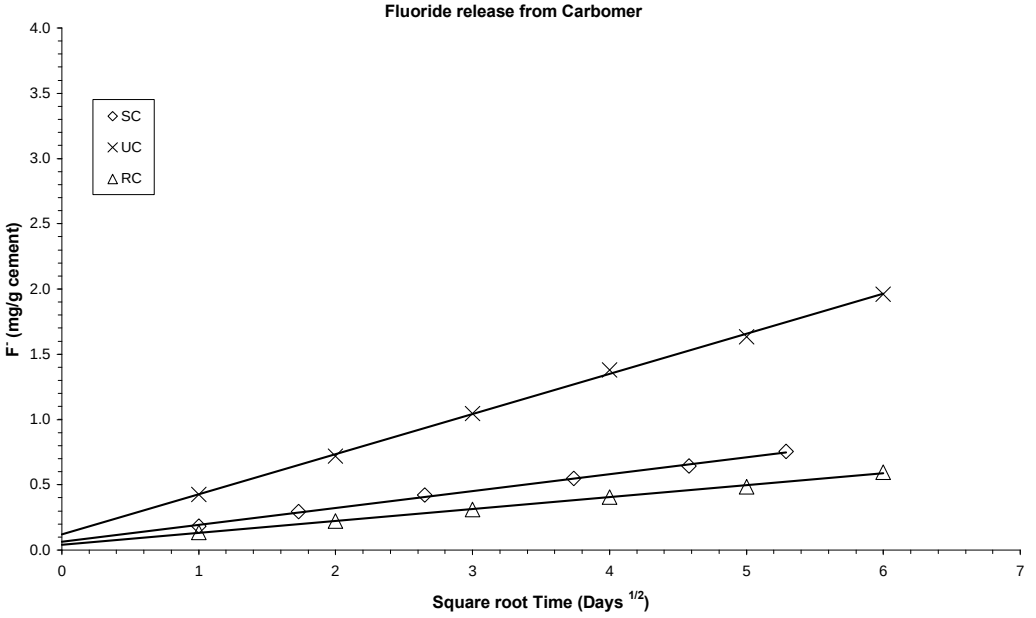


Figure 4.3: Cummulative fluoride release from Glass Carbomer.

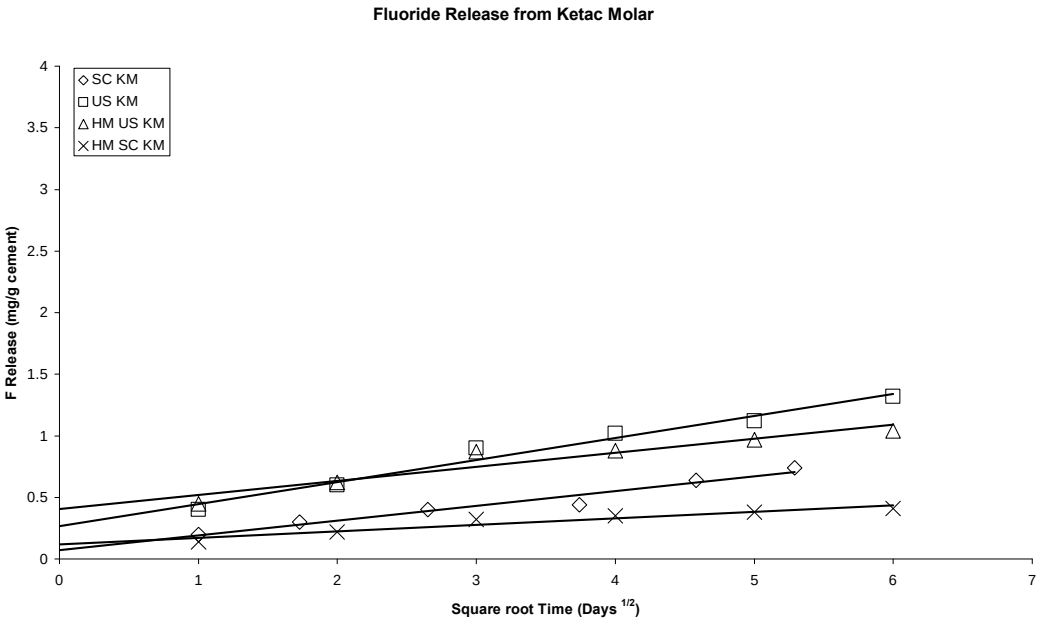


Figure 4.4: Cumulative fluoride release from Ketac Molar

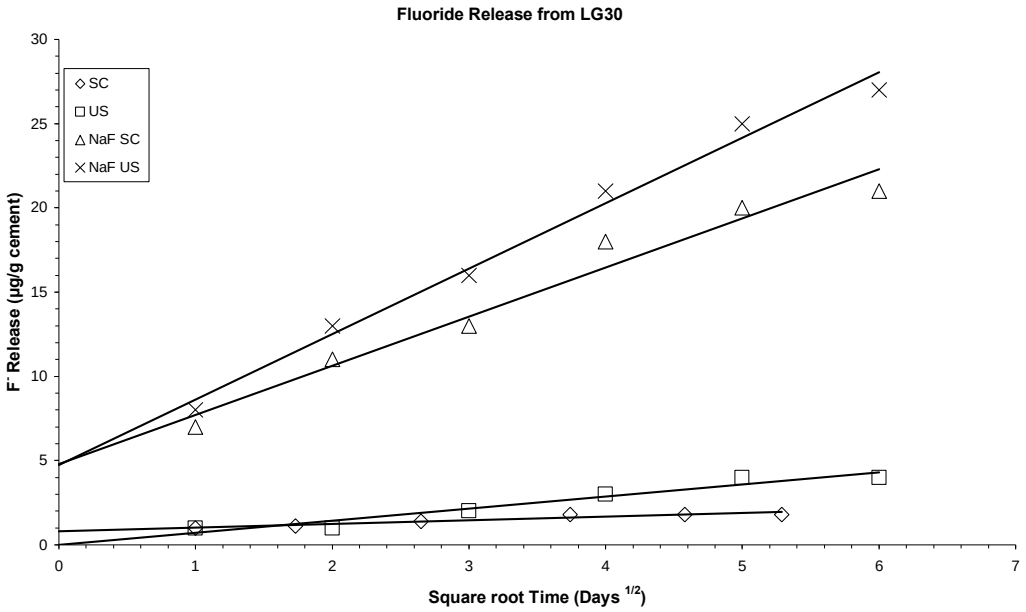


Figure 4.5: Cummulative fluoride release from LG30 (Note: graph is in µg/ g cement).

Table 4.5: Effect of UC versus SC on slope (m) and intercept (c) of KM and FIX

	Material	HM	CM
On m	**KM**	206%	177%
	FIX	244%	381%
On c	**KM**	381%	286%
	FIX	139%	152%

Table 4.6: Effect of hand mix versus cap mix on m and C of KM and FIX

	Material	SC	UC
On m	**KM**	185%	166%
	FIX	146%	227%
On c	**KM**	83%	63%
	FIX	55%	152%

Table 4.7: Effect of UC versus SC on slope (m) and intercept (c) of Amalgomers

	AM HM	AM CM	AMCR CM
On m	213%	302%	279%
On c	298%	383%	108%

Table 4.8: Effect of capsule mixing versus handmixing on slope (m) and intercept (c) of Amalgomer

	SC	UC
On m	78%	110%
On c	95%	122%

Table 4.9: Cap mixed AM versus AMCR: Effect of ceramic addition on slope (m) and intercept (c)

	SC	UC
On m	146%	135%
On c	722%	308%

Table 4.10: UC versus SC: Increase in of slope (m) and intercept (c) (Note values are in μg)

	LG30	LG30 +NaF
On m	385%	133%
On c	~0.00	98%

Table 4.11: Effect of addition of NaF to LG30 on slope (m) and intercept (c) (Note: values are in μg)

	SC	UC
On m	1554%	539%
On c	560%	V. LARGE

4.4 Discussion

Results for all restorative commercial GICs show ultrasound to enhance F-release. This is in line with Rusche and Towler's findings (2006) for luting GICs. In both studies the release rate is linear with respect to $t^{1/2}$ indicating a diffusion controlled mechanism. In no instance is there any indication that the UC enhancement falls off with time. In this study good linearity is observed up to 28 days and in Rushe and Towler's case 90 days. In this study their results re-plotted against $t^{1/2}$ show that both intercept *m* (which represents the initial burst release) and slope *C* (which represents the long term sustained release) the of the best fit equation: $[F] = m\ t^{1/2} + C$ are increased for the commercial luting cements Ketac Cem and Fuji I. Our study of the equivalent restoratives KM and FIX show the same effect but m and C are generally increased much more in this study. Their increases for m were 140% for Fuji I and 122% for Ketac Cem and 220% and 200% for C. The lesser effect may reflect either the lower glass content of the luting cements or the longer duration of ultrasonic irradiation in this study. This was selected as optimal from a study in the conversion of carboxylic acid groups to carboxylate salt groups using ATR-FTIR (Talal *et al.* 2009). The increase in both m and C suggests that more fluoride is available for release rather than increased diffusion as the major effect. Rushe and Towler discussed possible causes of enhanced fluoride release and suggest the most likely explanation is enhanced reaction due to greater glass surface area available for reaction. They cite reduction in mean particle size due to cavitation (Towler *et al.* 2003). Their general conclusion is in line with our findings for m and C and those of

Talal *et al.* (2009) on carboxylate conversion. Further evidence of this is provided by the results on LG30 + NaF. The average effect of UC on m in this study is to increase it by 159% (X2.59) and C by 167% (X2.67) compared to SC for all commercial materials in this study (Tables 4.5-4.11). The Rushe and Towler values (2006) increase 30 and 111%, respectively. In contrast, for LG30 +NaF m increases by only 33% and C decrease by 2%. (Table 4.10). It therefore seems likely that UC has a small effect on diffusion from the cement matrix into the surrounding water and a larger effect on fluoride ion release into the matrix from the glass. Additional evidence in support of this hypothesis is provided by the results from the LG30 controls. Although, the formulation is designed to be fluoride free impurity levels of fluoride were found on analysis by Williams *et al*. (2003) (as shown in Table 4.1). The increase in m produced by UC is much higher than that produced by UC on the formulation with NaF. (The effect of UC on C did not change.) It therefore seems that most effect of UC is on fluoride ion release from glass into the polyacid matrix although release may be into the depleted layer around glass particles from which release occurs more easily into water than from the non-acid-treated particles (Williams *et al.* 2002; Luo *et al.* 2009).

The effect of capsule mixing on fluoride release is very variable. Two of the three materials show increased m for capsule mixed SC compared to hand mixed, whereas for UC all three show increases. All three comparisons show reduced values of C for SC whereas two of them show increases for UC (Tables 4.6 and 4.8).The effect of

method of mixing on F-release has not been subjected to much study, only a poster presentation at BSDR 2005 dealt with effect of porosity on fluoride release and uptake (Yan *et al.* 2005) and Verbeek *et al.* (1993) showed considerable increase in both short and longer term release for capsule mixing but for only one material.

Looking at the interaction between method of mixing and effect of UC for FIX and Amalgomer the UC effect is enhanced for both m and C. For KM it is reduced slightly for m but by 24% for C. In a previous study Jones *et al.* (1997) have indicated higher levels of porosity in FIX than in KM. This may therefore suggest that porosity reduction may be a factor influencing the difference observed.

The results for glass GC when self cured are very similar to the other GICs tested in this study. The siloxane incorporation into the material referred to in the manufacturer's patent does not produce any marked difference in the type of [F] v t_ plot produced. The level of enhancement by UC of m and C is also similar. The interesting feature of this product is the manufacturer's advocacy of the use of a dental curing light with appreciable radiant heat output to accelerate the set. Using the curing light recommended for their specified duration produced reductions in m and C compared to SC. These results are the only ones comparing the effect of heat and ultrasound on F-release. The effects on compressive strength are reportedly similar on other GICs, i.e. both produce enhancement compared to SC (Kleverlaan *et al.* 2004). Examining the conversion of the ratio of carboxylic acid to carboxylate peaks (as

described in Talal *et al.* 2009) shows 187% increase for UC compared 157% for RH after 10 min. After 60 min they are similar UC 187%, RH 195% and SC is 192%. Though not a direct comparison Rushe and Towler (2006) showed UC enhanced fluoride release whereas Woolford and Grieve (1995) showed reducing levels with increasing duration of infrared radiation. This comparison therefore provides direct evidence that UC produces effects other than those arising from the heat that is generated in its application to GIC.

The results of Amalgomer and Amalgomer CR provide the direct comparison between a GIC and a similar material with a secondary filler 19.7% ZrO. Although the secondary filler is fluoride free and replaces an appreciable proportion of the fluoride containing glass the effect on fluoride release is higher both for SC and UC. Particularly surprising is the relative effects on m and C (Table 4.9). The larger effect is on C suggests that the initial ‘‘wash out’’ is greater. Previous studies with GICs having secondary fillers have been of GICs having very large weight percentages of silver or silver tin alloy (Mallak and Sarkar, 1990) and showed reduced fluoride release. GC contains fluorapatite as secondary filler but no material without this present was available for a comparison to be made.

Since the composition of all the commercial GIC glasses had been determined it was possible to evaluate the effects of Na and F content on the F-release both as m giving a measure of diffusion controlled continuing release and C as a measure of

initial “burst” or “washout” behaviour. NOTE this was not a primary objective of this study and the effects would be confounded by other factors such as method of mixing, presence or absence of secondary filler, and different polyacids. Also the F-contents had a more limited range (9.0-13.3%) for F as contrasted to (1.0-5.3%) for Na. (The results for LG30 were excluded since it had a negligible F content and would therefore have had no F release thus skewing the statistics.)

Table 4.12: Effect of F and Na content of glass on F-release Values of R^2 from linear correlations with m and C

Cure type	Element	m		C	
SC	Na	0.66	(p=0.05)	0.88	(p=0.01)
UC	Na	0.53	(p>0.05)	0.12	(p>0.05)
SC	F	0.07	(p>0.05)	0.24	(p>0.05)
UC	F	0.001	(p>0.05)	0.14	(p>0.05)

Table 4.12 shows the correlation coefficients (in the form of R^2) from linear regression analysis. All values of R were positive but only the effects on m and C of Na for SC samples were statistically significant. The correlations were always weaker for UC than for SC. The absence of positive link between F content (in the range used in commercial dental GICs) and F release has been reported previously (Meryon and Smith, 1984). The correlation for C and Na was particularly strong. This is in line with findings with glasses where only the Na content of the glass was varied (Hill *et al.* 1995). Although values of m and C were not determined in that study, the initial release over 64 hours increased much more than the subsequent cumulative release from 64 hours to12 weeks. The release relative the Na-free glass rose from 15% for

0.3% Na to 130% for 1.2% Na for initial release as contrasted with -12% to +39% for subsequent cumulative release.

4.5 CONCLUSIONS

Ultrasound accelerated setting enhances fluoride release from GICs. Heat accelerated setting has an opposite effect. This confirms that heat generated by UC is not its only effect where the fluoride content of the GIC is present in the water of the GIC rather than in the glass the effect of UC is much less indicating that UC acts on F-containing GICs to enhance fluoride release from the glass component. The effect of HM compared to capsule mixing on fluoride release is not in a consistent direction. The presence of inert Zirconia secondary filler enhances fluoride release although the fluoride content is reduced. The Na content of the glass enhances initial fluoride release more than subsequent release rate.

CHAPTER 5

THE ROLE OF GLASS COMPOSITION IN THE BEHAVIOUR OF GLASS ACETIC ACID AND GLASS LACTIC ACID CEMENTS

The role of glass composition in the behaviour of glass acetic acid and glass lactic acid cements. J Mater Sci Mater Med. 2008 Feb;19(2):541-5.

5.1 Introduction:

Unlike the other dental cements, GICs show changes in physical properties over prolonged periods (i.e. > 24 hours). In an attempt to study this change in long term properties, Wasson and Nicholson (1992) made model cements using GIC glass mixed with acetic acid solution (replacing poly(acrylic acid). For the first few hours the cement formed was not hydrolytically stable but after 24 hours it resisted water.

From this they deduced that some other setting mechanism might also occur since the acetates of all the cations (i.e. Na, Ca, & Al) were readily soluble. More recently Nicholson and Czarnecka have evaluated model cements using lactic acid in place of acetic (Nicholson *et al.* 2002; Nicholson and Czarnecka 2004). The mechanisms discussed involve the production of a complex silicate polymer network. Matsuya *et al* (1996) reported changes in both infrared and NMR spectra which appeared to support the formation of this secondary silicate network in the GIC matrix phase. More recently, De Maeyer *et al*. (2002) using infrared spectroscopy on the glass phase alone found that effect of acid on this component could account for the spectral changes observed. In addition, the particular glass used with both acetic acid and lactic acid (Wasson and Nicholson, 1993; Nicholson *et al*. 2002; Nicholson and Czarnecka, 2002) had certain characteristics that made it unsafe to draw general deductions from results obtained on it alone. Although commercially successful glass ionomer dental restorative cements have been based on this glass (G338) they do not show changes in either compressive or flexural strength at periods >24 hours (Brune

1982; Towler *et al* 2001). The composition of G338 is not entirely typical of other GIC glasses as it has high levels of both F and P. Both elements can form anions which have insoluble salts with Ca and Al.

To elucidate the possible role of silicate network formation this study aims to compare the behaviour of G338 glass with that of MP4 which is a simple oxide glass containing 28%SiO_2; 35%Al_2O_3 ; 26%CaO; 11%Na_2O. Although cements based on MP4 were developed for orthopaedic splinting where hydrolytic stability was not needed, these cements are known to be perfectly stable in water (Hadley *et al*. 2000) and have been used in comparisons with dental glass ionomers.

Since this glass contains neither F nor P the potential for insoluble salt formation, apart from silicate is eliminated. The objectives are to evaluate the hydrolytic stability of the reaction products formed from the two glasses each with acetic and lactic acid and to examine the effects of maturation time on all four materials. In addition the infrared spectra will be evaluated to compare with those reported by De Maeyer *et al*. (2002).

5.2 Fourier Transform Infrared spectroscopy:

Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Infrared spectroscopy

detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. For example, the C=O stretch of a carbonyl group appears at around 1700cm^{-1} in a variety of molecules. Hence, the correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample. The wavenumber positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules. Thus the presence of specific functional groups can be monitored by these types of infrared bands, which are called group wavenumbers.

5.3 Attenuated total reflection (ATR-FTIR) technique

An alternative to transmission mode spectroscopy is the ATR-FTIR technique. This technique is widely used by researchers to examine a variety of sample types including solids, powders, pastes, liquids, polymers and thin films. It is also suitable for characterization of materials which are either too thick or too strong absorbing to be analyzed by transmission spectroscopy. For the bulk material or thick film, no sample preparation is required for ATR analysis.

For the attenuated total reflection infrared (ATR-IR) spectroscopy, the infrared radiation is passed through an infrared transmitting crystal with a high refractive

index, allowing the radiation to reflect within the ATR element several times. The sampling surface is pressed into intimate optical contact with the top surface of the crystal. The IR radiation from the spectrometer enters the crystal. It then reflects through the crystal and penetrating "into" the sample a finite amount with each reflection along the top surface via the so-called "evanescent" wave. At the output end of the crystal, the beam is directed out of the crystal and back into the normal beam path of the spectrometer.

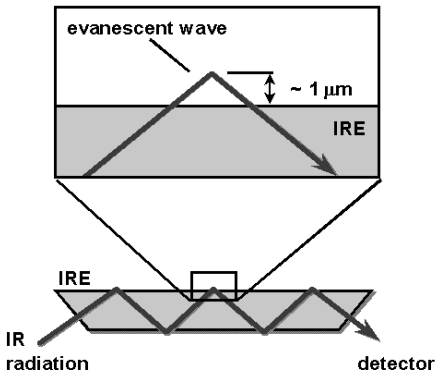


Figure 5.1: Total internal reflection at the interface of an internal reflection element. Depth of penetration of the evanescent wave is approximately 1 mm.

5.4 Materials and Methods

5.4.1 Materials:

5.4.1.1 Glasses:

Two glasses, MP4 and G338 were selected for use in this experiment. Compositions of these glasses are shown in table 5.1.

Table 5.1: Elemental composition for G338 and MP4 (percentage by weight)

Glasses	Elements						
	Al	**Ca**	**F**	**Na**	**O**	**P**	**Si**
G338	16.9	6.6	19.7	6.3	32.5	6.2	11.8
MP4	18.5	18.6	-	8.2	41.6	-	13.1

MP4 is a fluoride and phosphate free glass. However relative to G338 it contains a higher percentage of Al, Ca, Na and Si. MP4 is a simple oxide glass and was developed for orthopaedic splinting.

G338 glass was developed for use in dental glass ionomer cements. It is also a commercially used glass and contains both fluorine and phosphorus.

Particle size analysis was performed on both the glasses using Malvern Particle Size analyzer. G338, being of a larger particle size, was ball milled for 48 hours to

produce a particle size similar to that of MP4. After milling G338 was sieved using a <20 micron sieve to produce glass of regular particle size distribution.

4.4.1.2 Cements:

For cement formation lactic and acetic acid were used at a concentration of 75% and 45% respectively.

Lactic Acid cements:

Cements for lactic acid were prepared using a P:L ratio of 3:1. Glass and acid were mixed on a glass slab for not more than 30 seconds. After this the cement was packed into moulds to produce disks measuring 10mm in diameter and 1 mm thick. Four discs were prepared in this manner. A disk was allowed to mature for either 1, 2, 3, 6 or 24 hours. After these times the cement disk was dropped into 40ml of deionised water to asses its hydrolytic stability by visual examination the procedure for which is described later.

To observe salt formation, ATR-FTIR analysis was performed using Perkin Elmer Infrared spectrometer.

Acetic acid cements:

Acetic acid cements were prepared in the same manner as lactic acid cements. However a P:L ratio of 4:1 was used for cement formation.

5.4.2 Methods:

5.4.2.1 Particle size analysis:

The procedure for particle size analysis is similar to that described earlier section 3.4.2.1

5.4.2.2 ATR-FTIR Analysis

ATR-FTIR was performed on Perkin Elmer Spectrometer using Spectrum 2000 software. The wavelength range was set between 1800 cm^{-1} and 700 cm^{-1}. To minimize the error four scan cycles were used for each reading. Before taking the sample readings, a background spectrum was obtained. This is a single beam spectrum recorded without placing sample on the machine. Spectra were recorded in the absorption mode.

Spectra were obtained for both Lactic acid and Acetic acid to compare with the spectra of mixed cements.

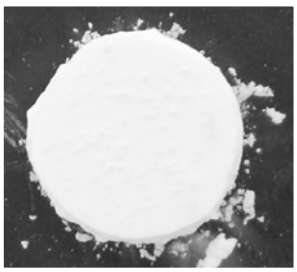
The cement mix was placed onto the ATR window soon after mixing and then spectra were generated at 1,2,3,6 and 24 hours. Each spectrum was superimposed onto the previous one to observe a change. No change in the spectra was taken as completion of the acid-base reaction with no further salt formation.

5.4.2.3 Assessment of Hydrolytic stability:

Assessment for hydrolytic stability of cements was performed by visual examination based on a point scale system (table 5.2). Based on the stability, each cement was given a score after the predetermined time intervals. At the end of 24 hours the score was then totalled for each type of cement to see how the cement had performed. A higher score showed the least hydrolytic stability and the vice versa.

Table 5.2: Point system for hydrolytic stability

Score	Features
1/5	Fully intact
2/5	Fully intact with minor surface defects including minor fissures
3/5	Massive fissuring but no disintegration
4/5	Disintegrates into large chunks
5/5	Disintegrates into fine powder



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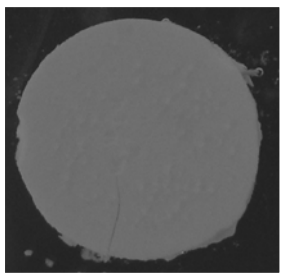

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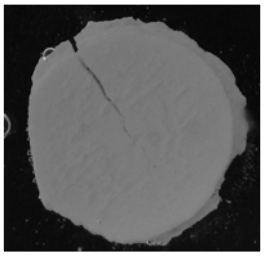

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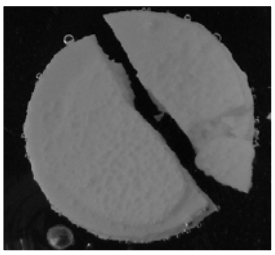

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5.5 Results:

5.5.1 Particle size analysis:

Results for particle size distribution for both G338 and MP4 is shown in table 5.3. It may be noted that both the glasses show a similar particle size distribution.

Table 5.3: Results for particle size analysis.

Glasses	Particle size (μm)		
	D 90	**D10**	**D50**
G338	13.43	0.93	3.29
MP4	12.43	0.46	3.99

5.5.2 ATR-FTIR Spectra:

Spectra for lactic acid and acetic acid show the presence of an C=O peak at ~1700 cm^{-1} (Figure 5.3 and 5.4). On mixing with glass this peak steadily decreased with the formation of acetate and lactate salts. Peaks for acetate salts appear at ~1550 cm^{-1} and ~1615 cm^{-1} (Wasson and Nicholson, 1993) whereas peak for lactate salts appear at ~1604cm^{-1} (Nicholson *et al.* 2002) It was noted that for both lactic acid and acetic acid cements of G338 and MP4 there was rapid salt formation until 3 hours after which there was no substantial change in the spectra (Figure 5.5).

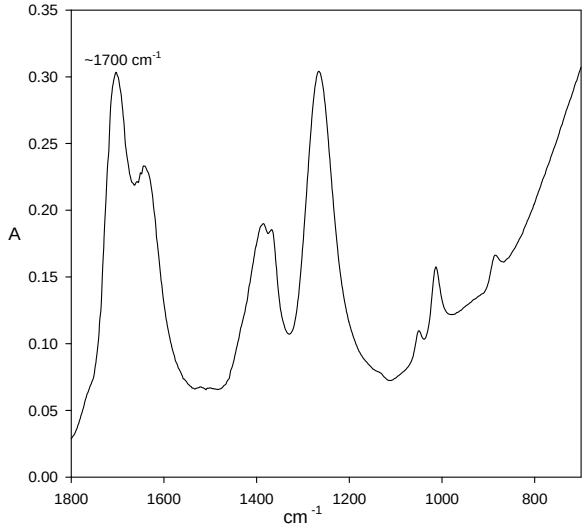

Figure 5.3: ATR-FTIR Spectrum for 45% acetic acid showing C=O peak at ~1700 cm^{-1}

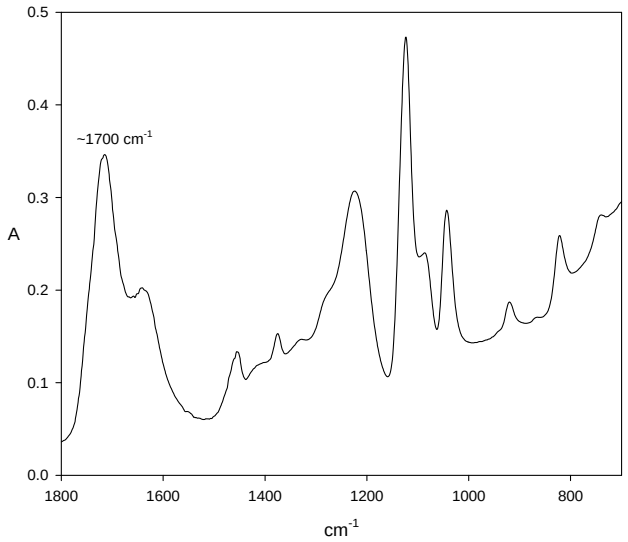

Figure 5.4: ATR-FTIR Spectrum for 75% lactic acid showing C=O peak at ~1700cm^{-1}

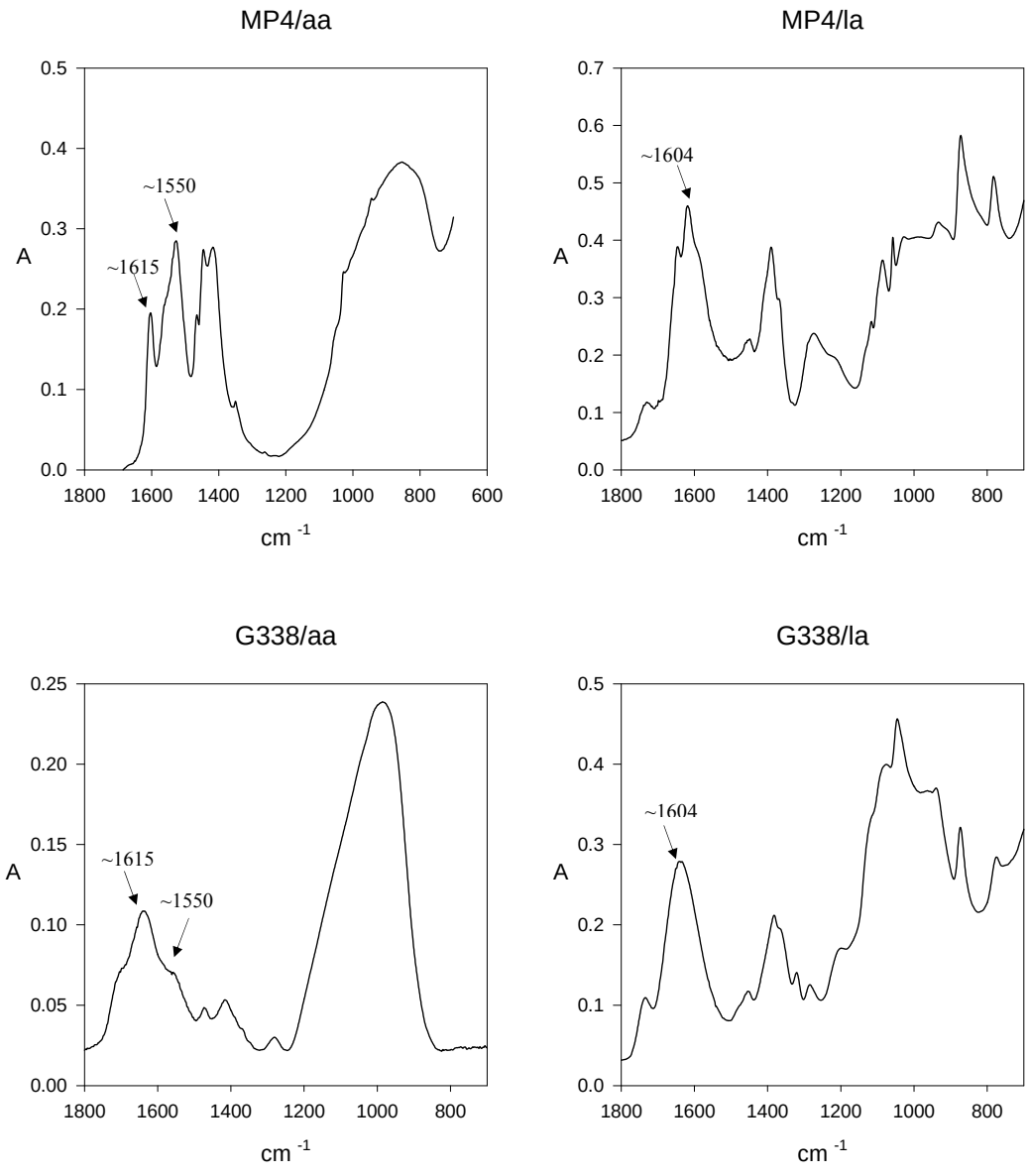

Figure 5.5 FTIR-ATR scans at 6 hours (aa= acetic acid cements; la=lactic acid cements)

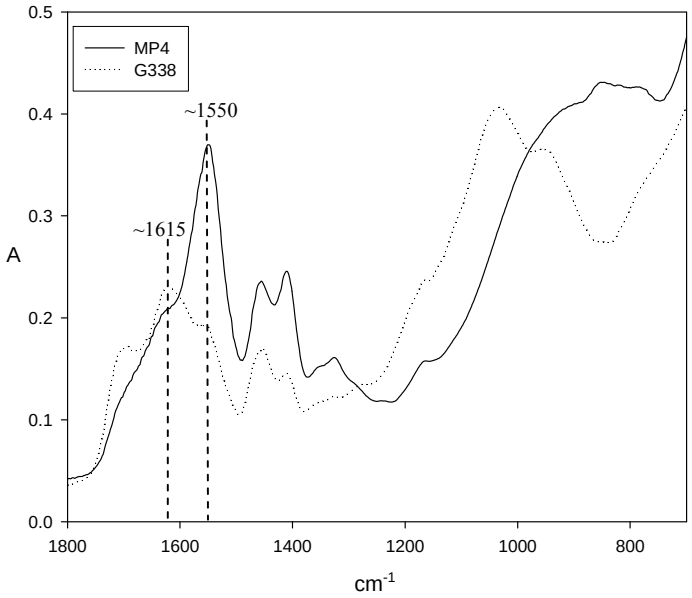

Figure 5.6: ATR-FTIR spectra for G338 and MP4 cements with PAA taken after one hour of setting.

Figures 5.6 show the spectra obtained by the reaction of G338 and MP4 with po(lyacrylic acid). On comparing these with the spectra obtained for lactate and acetate cements it can be observed that acetate cements are more characteristic of the polyacrylate cement.

5.5.3 Hydrolytic stability:

Results for hydrolytic stability are shown in Table 5.4.

Table 5.4: Hydrolytic stability based on point score system.

	1	2	3	6	24	Total points
G338 (lactic)	4/5	4/5	2/5	2/5	2/5	2.8
MP4 (lactic)	1/5	1/5	1/5	3/5	2/5	1.6
G338 (acetic)	4/5	4/5	1/5	1/5	1/5	2.2
MP4 (acetic)	5/5	5/5	5/5	5/5	5/5	5

G338:

G338 cements were hydrolytically stable when allowed to mature for at least three hours at room temperature. After three hours G338-acetate cement was more resistant to water attack than G338-lactate cements. Although G338-lactate cements maintained their disk like shape after, they showed minor surface changes including minor surface fissuring.

MP4:

MP4 showed the best hydrolytic stability as a lacate cement where as it had the lowest hydrolytic stability as acetate cement. MP4-lactate cements matured for only one hour, remained fully intact when dropped in water. The same was observed for cements matured for 2 and 3 hours. However, quite interestingly, MP4-lactate cements matured for more than 3 hours were susceptible to develop surface defects on dropping in water.

MP4-acetate cements, on the other hand, did not produce hydrolytically stable cements when matured for any length of time and were the least hydrolytically stable cements of all. These cements instantly disintegrated into fine powder on dropping into water and continued to do so even when allowed to mature for 24hours.

5.6 Discussion

5.6.1 Choice of materials and methods

5.6.1.1 Glasses

Glasses used in this experiment were G338 and MP4. Both are commercially used glasses where MP4 is used in splinting and G338 is a component of glass ionomer for dental use. G338 has a high content of fluoride and phosphate whereas MP4 is a fluoride and phosphate free simple oxide glass. Using G338-acetate cements Wasson and Nicholson concluded that a silicate phase is responsible for the maturation of glass ionomer cements, however both phosphate and fluoride have a tendency to form anions which have insoluble salts with calcium and aluminium. To fully elucidate the role of silica in maturation it was considered essential to use a glass which does not have any fluoride and phosphate and hence MP4 was selected for use in this experiment.

5.6.1.2 Acids

Lactic and acetic were used in this experiment as previously described by Wasson and Nicholson. Calcium and aluminium form soluble salts with lactic and acetic acid.

In the conventional glass ionomer cement both these cations are responsible for the cross linking of poly(acrylic acid) chains by forming insoluble salts. Using alternative acids, as done in this experiment, helps understand if another phenomenon apart from calcium and aluminium cross linking plays a role in the setting mechanism of glass ionomer cements.

5.6.1.3 P:L ratios

The P:L ratio selected for use in this experiment were those use by Wasson and Nicholson in their study. Their work showed that these P:L ratio produce cements with optimum strengths.

5.6.1.4 Particle Size analysis:

A discussion for this method is already given in section 3.6.1.4.

5.6.1.5 FTIR analysis:

Setting reaction in terms of salt formation was analysed using ATR-FTIR 'Golden Gate Technique'. The golden gate method is very suitable to determine the stages of cement setting and is more sensitive than other techniques (Nicholson *et al*. 1988). It enables spectra to be generated after specific time intervals with very short scan time. FTIR shows different peaks corresponding to specific salt formation.

The limitation of this technique is that only the surface in contact with the ATR diamond can be analysed it does not produce readings for the bulk of the sample.

Another limitation of the ATR-FTIR technique is that as the material sets it contracts away from the diamond window so the knob of the apparatus has to be tightened in order to maintain a good contact.

5.6.2 Analysis of Results

The results on acetic acid cements demonstrate the hypothesis that maturation of GICs is caused by formation of a silicate network in the polyacid matrix is not viable. MP4 contains the same amount of silica as G338 but does not form insoluble cement with acetic acid. In contrast, G338 does behave in this way as reported previously by Wasson and Nicholson (1993). Examination of the differences between MP4 and G338 (table 4.4) show other elements present in the latter that may account for the formation of hydrolytically stable cements. Both P and F are present in high levels (compared to most GIC glasses). If the initial formation of soluble acetates occurs with acid attack on the glass, as the pH increases these elements may provide anions that could precipitate calcium salts. CaF_2 is very insoluble as are various phosphates such as hydroxyapatite or fluorapatite. The formation of such compounds is analogous to the processes involved in the setting of Zinc Phosphate and Dental Silicate Cement materials.

The behaviour of lactic acid based cements differs from acetic acid based ones. This is not surprising as lactic acid is not as weak an acid as acetic [pKs of 3.86 and 4.76

respectively]. Also lactic acid has the possibility forming chelate structures. This difference is clearly indicated in the FTIR spectra which have peaks in areas not shown by acetic acid cements or GICs (see fig 4.5). In contrast to acetic acid and polyacid in cements the lactic acid concentration used here (the optimum found by Nicholson and Czarnecka (2004) is much higher. Calcium lactate is only moderately soluble (Wilson *et al*.1981). As Nicholson and Czarnecka (2004) state in their investigation of lactic acid based cements, "Following our recent work on the interaction of aqueous lactic acid with set glass-ionomers we have become interested in the possibility of forming cements from glass and this acid only…" Although the lactic acid cements have been evaluated as a direct comparison between the behaviour of G338 and MP4 glasses, the lactate cements are plainly not models for GICs in the way that acetic acid (Wasson and Nicholson, 1993) or propionic acid (Wiiliams *et al*. 2002) ones are; nor were they intended as such.

The most interesting aspect of this study is the comparison of MP4 cements with the two different acids. The total failure to form hydrolytically stable cements with acetic acid contrasts with the initial hydrolytic stability of the lactate cements. This latter is a very unusual phenomenon, most dental cements exhibit the reverse behaviour. It would appear that the relatively early exposure to water enhances the cements stability. Possibly the cement may take up water to produce an improved structure; as noted above the lactic acid concentration is very high. The initial hydrolytic stability

of the MP4:lactic acid cement suggest that it may have a possible application as a temporary dental cement.

The setting reaction as shown by FTIR traces (fig. 5.5) is similar to those found when GICs are examined by this technique. De maeyer *et al*. (2002) reported that G338 treated with acetic acid showed silicate related absorption peaks at 800cm-1 and 1073cm-1 but the former is not shown in our study and the latter would be masked by the carboxylate peaks at 1000cm-1 (fig 4.5). Our findings agree with the conclusion of De Mayear *et al*. (2002) that the "silica gel phase is formed as a surface layer on the glass particles and not as a hydrated silicious matrix…." (Demayer *et al*. 2002)

5.7 Conclusions

Within the limits of this study it can be concluded that theories related to the maturation of glass ionomer cements require revision. Silica alone does not seem to be the only mechanism involved in cement stability.

It is clearly evident that the stability of acetate cement is determined by the composition of the glass. In order to understand which of the glass componenets are responsible for the stability of these cements, it is essential to use a variety of glasses with different compositions.

CHAPTER 6

SECONDARY SETTING REACTION IN GLASS IONOMER CEMENTS: HYDROLYTIC STABILITY OF ACETIC ACID CEMENTS

Presented at BSDR Glasgow, 2009

6.1 Introduction

Glass ionomer cements (GICs) are widely used as dental restorative materials. An important factor concerning their clinical performance is the effect of maturation at times greater than 24 hours on their physical properties (Pearson and Atkinson, 1991; Williams *et al*. 1989; Williams *et al*. 1991; William *et al*. 1992; De Gee *et al*. 1996). Mechanical strength (Pearson and Atkinson, 1991; Williams *et al*. 1989; Williams *et al*. 1991), hardness, and resistance to abrasion and erosion (Williams *et al*. 1992; Billington *et al*. 1992; De Gee *et al*. 1996) improve for some or all GICs. The structural changes in the GIC resulting in these changes has not been unequivocally identified. The initial setting mechanism of GICs is shown to be by acid attack on the glass particles resulting in release of cations such as Al^{3+} and Ca^{2+} which interact with the carboxylate groups on the polymer component to produce ionic crosslinks. Additional crosslinks may form to account for the changes observed. This may occur because of continuing release of these ions from the glass, conformational changes in the polymer making additional carboxyl groups accessible to form crosslinks, or by replacement of Ca by Al (Crisp and Wilson, 1974; Crisp and Wilson 1976). It has been previously suggested that replacement of Na carboxylate non-crosslinking groups by Ca, Al or other crosslinking species might account for the effect (Billington *et al*. 2006). It is, however, not the only mechanism as some formulations free of Na or any other monovalent cations former do show increases in strength after 24 hours. Other potential explanations offered relate to the water content of the cement; conversion of “free” to “bound” water showing a correlation with increased

strength over a range of cements (including GIC) (Young *et al*. 2000). One particularly interesting explanation suggests that maturation changes are caused by a silicate network forming in the ionically crosslinked polyacid matrix (Wasson and Nicholson, 1992). This hypothesis was derived from the behaviour of glass acetic acid cements models of GICs. Wasson and Nicholson suggested that since these cements have no possibility of forming ionic crosslinks and the acetates of Al and Ca are reportedly very soluble (Wasson and Nicholson, 1992) the observation that the cements formed become hydrolytically stable with time was claimed to support the idea of an inorganic polymer network of silica forming. However Mehrotra and Bohra (1983) report that the acetate of aluminium are insoluble in water. In a recent paper it has been demonstrated that whilst the glass used did form a hydrolytically stable acetate cement, using a glass with a comparable silica content did not form hydrolytically stable acetate cement (Shahid *et al*. 2008). We therefore suggested that one possible explanation was the precipitation of aluminium or calcium salts of phosphate or fluoride released from the glass as the pH changed in the cement. The objective of this study was to investigate the hydrolytic stability of acetate cements formed from other glasses. Particularly we aimed to compare glasses which had only F or P with a similar one with both. Additionally the hydrolytic instability of MP4 acetate cement could be due to its high Na content. We therefore decided to evaluate acetate cement formed from a glass without Na as well as neither F nor P. To elucidate the mechanism responsible for cement hydrolytic stability, NMR spectra of

the cement and ICP analysis of the water in which the cement was immersed during hydrolytic stability testing were carried out.

6.2 Nuclear Magnetic Resonance

Nuclear magnetic resonance, NMR, spectroscopy is a technique used to study the structure of materials. When an atom is exposed to a magnetic field, the energy level in the atom splits into several energy states and this process is known as the Zeeman effect. The number of energy states is given by $2I+1$, where I is the spin quantum number, and spin quantum number is highly dependent on the number of unpaired protons and neutrons in the atom.

The magnetic nuclei spread according to the Boltzmann distribution in the allowed energy states. In the NMR experiment, a short and an intense burst of radiofrequency radiation is applied to the sample. This will excite the magnetic nuclei, and the nuclei in the lower energy level excite to the higher energy level. An NMR spectrum can be recorded if the difference in the energy states is the same as the applied frequency (Hore, 1995).

The energy required is dependant on the chemical shielding and the local environment of the nucleus. Thus solid state NMR probes the local environment of the nucleus and gives information on local bonding and co-ordination states.

Samples used for NMR in this study were in powder form, and therefore, it is necessary to perform NMR in the solid state. In the solid state, there are interactions within the material, which are angular dependent such as chemical shielding, dipole-dipole coupling, and quadrupole coupling. In the solution state, however, the molecular motion is fast enough to overcome these angular dependent interactions. These angular dependent interactions can result in line broadening of NMR spectrum. To solve this problem, samples are run at 54.7 degrees with respect to the direction of the magnetic field, and this angle is known as the magic angle.

6.3 Materials and Methods

6.3.1 Materials

6.3.1.1 Glasses

Five glasses were selected for use in this experiment. Compositions of these glasses are shown in table 6.1

Table 6.1: Elemental composition for glasses (percentage by weight)

Glasses	Elements						
	Al	**Ca**	**F**	**Na**	**O**	**P**	**Si**
G338	16.9	6.6	19.7	6.3	32.5	6.2	11.8
MP4	18.5	18.6	-	8.2	41.6	-	13.1
LG30	15.0	18.6	0.0	0.0	45.4	9.3	11.7
LG117	13.0	25.6	6.1	0.0	38.4	0.0	16.9
LG26	14.4	20.6	6.7	0.0	38.4	8.6	11.3
Anorthite	19.4	14.4	0.0	0.0	46.0	0.0	20.2
Na Anorthite	15.9	11.8	0.0	6.8	44.8	0.0	20.7

MP4 is a fluoride and phosphate free glass. However relative to G338 it contains a higher percentage of Al, Ca, Na and Si. MP4 is a simple oxide glass and was developed for orthopaedic splinting.

G338 glass is developed for use in dental glass ionomer cements. It is also a commercially used glass and contains both fluoride and phosphate.

LG26, LG117 and LG30 are Limerick glasses which differ in their fluorine and phosphate content. LG26 contain both fluorine and phosphate where as LG117 is phosphorus free, whilst LG30 is fluorine free but contains phosphorus.

Anorthite is a simple oxide glass and Na-anorthite is a sodium conating glass which is based on the anorthite composition.

Particle size analysis was performed on all the glasses using Malvern Particle Size analyzer. This was done to ensure they were of a similar particle size

6.3.1.2 Cements

Cements were formed as described earlier in section 5.4.1.2.

6.3.2 Methods

6.3.2.1 NMR Analysis

Cements were allowed to set for 24 hours at room temperature after which they were dropped into liquid nitrogen to stop the reaction. The cements were then ground using mortar and pestle. The ^{27}Al NMR measurements were carried out at the 600MHz Bruker NMR spectrometer with the magnetic field strength 14.1 T, at a resonance frequency of 156.3 MHz. The rotor was spun at 15-21 kHz. The short pulse was applied corresponding to $\pi/12$ of the magnetization tip angle. The recycle delay was 0.5 s. The ^{27}Al NMR chemical shift was referenced to 0 ppm frequency of the signals in 1 M aqueous solution of $AlCl_3$.

6.3.2.2 ICP Analysis:

Cement discs were dropped in 40ml of deionosed water after they had set for 1 hour and 24 hours. They were allowed to remain in the water for 24 hours after which cement discs were taken out from the water. The water was then analysed for Al, SI, Ca, Na and P using ICP-OES spectrometer.

6.3.2.3 Assessment of Hydrolytic stability:

Assessment for hydrolytic stability of cements was performed by visual examination based on a point scale system (table 6.2). Based on the stability, each cement was given a score after the predetermined time intervals. At the end of 24 hours the score was then totalled for each type of cement to see how the cement had performed. A higher score showed the least hydrolytic stability and the vice versa.

Table 6.2: Point system for hydrolytic stability

Score	Features
1/5	Fully intact
2/5	Fully intact with minor surface defects including minor fissures
3/5	Massive fissuring but no disintegration
4/5	Disintegrates into large chunks
5/5	Disintegrates into fine powder

6.4 Results:

6.4.1 Hydrolytically stability:

Results for hydrolytic stability are given in table 6.3

Table 6.3: Results for hydrolytic stability of acetate cements

Time [hrs]	1	2	3	6	24
LG26	0.2	0.2	0.2	0.2	0.2
LG30	0.8	0.8	0.8	0.8	0.2
LG117	0.2	0.2	0.2	0.2	0.2
Anorthite	0.2	0.2	0.2	0.2	0.2
Na Anorthite	0.2	0.2	0.2	0.2	0.2
G338*	0.8	0.8	0.2	0.2	0.2
MP4*	1.0	1.0	1.0	1.0	1.0

All the LG glasses, with the exception of LG30 form stable cements at 1 hour and continue to do so upto 24 hours. LG30, on the other hand forms stable cement only after 24 hours.

From the "Anorthite group" both anorthite and Na-anorthite form hydrolytically stable cements from the very beginning.

5.4.2 Ion Release from Acetate Cements:

Release of ions from acetate cements after 1 hour and 24 hours of setting is given table 6.4. Silicon release decreases at 24 hours for all glasses whereas aluminium reduces at 24 hours except for LG30.

Table 6.4: Release of ions (mg/L) after 1h and 24 hours

Ions		Si	Al	Ca	P	Na
G338	**1h**	27.40	39.41	33.69	1.03	47.50
	24 h	*11.43*	*12.54*	*10.58*	*<0.01*	*27.79*
LG26	**1 h**	18.79	5.54	59.90	<0.01	0.72
	24 h	*9.53*	*0.12*	*46.28*	*<0.01*	*0.81*
LG30	**1 h**	5.95	20.93	45.28	3.04	<0.01
	24 h	*4.98*	*26.41*	*61.03*	*6.65*	*<0.01*
LG117	**1 h**	7.13	6.92	110.81	<0.01	0.87
	24 h	*4.49*	*2.55*	*119.12*	*<0.01*	*0.97*
Anorthite	**1 h**	3.80	10.55	22.48	<0.01	0.65
	24 h	*1.97*	*11.81*	*27.45*	*<0.01*	*0.73*

For anorthite the release of aluminium remains more or less the same. Release of aluminium after one hour is highest for the G338 cement followed by LG30 cement. Calcium release increases at 24 hours except for G338 and Anorthite.

6.4.3 ^{27}Al MAS-NMR

^{27}Al spectra for glasses (figure 6.1) shows the presence of a broad asymmetrical peak around 48-65 ppm, which is attributed to a tetrahedrally co-ordinated aluminium (Al (IV)) site in the alumino-silicate network (Engelhardt *et al*. 1985; Kirkpatrick *et al*.1985; Merzbacher *et al*. 1990; Stamboulis *et al*. 2005).

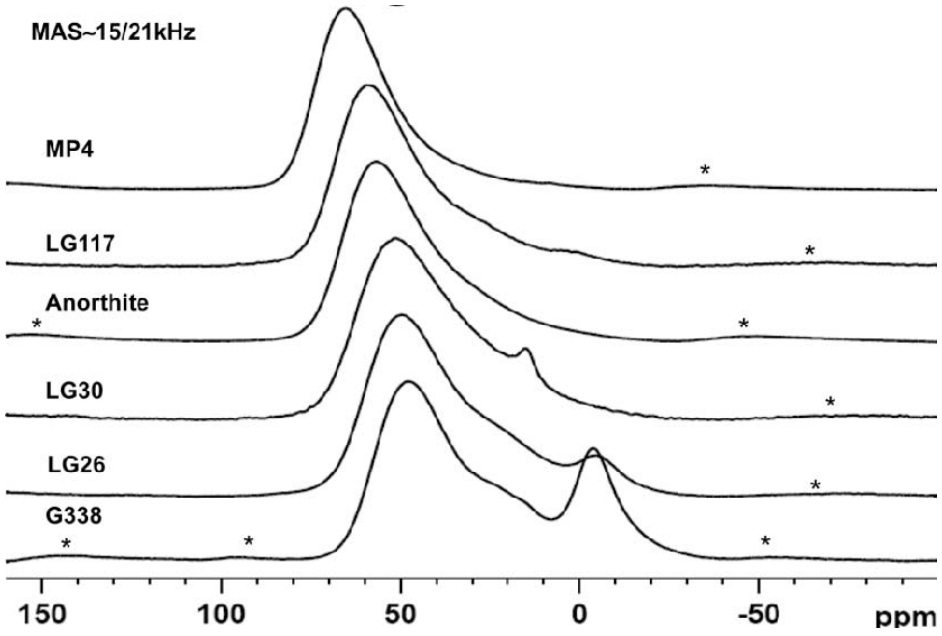

Figure 6.1: 27 Al MAS-NMR spectra for glasses used in acetate cement formation

The Al(IV) peak is present in all the glasses. For glasses without phosphate (MP4, LG117 and Anorthite) the chemical shift was found at 60ppm that corresponds to Si-O-Al bonds. However in the presence of phosphorus, this chemical shift moves slightly towards 0 ppm due to the formation of Al-O-P bond.

Another peak which appears near 0 ppm is attributed to the octahedrally co-ordinated Al(VI) species (Matsuya *et al*. 1996; Cong *et al*. 1993). This peak appears in G338, LG26 and LG117.

LG30 shows a peak near 15ppm which has been attributed to Al(V) species. Based on the data from Jakobsen *et al.* (1989) it can be estimated that the 27Al MAS-NMR signal from alpha-alumina should come at 14.5ppm. The sharp signal at 15ppm observed on the ^{27}Al MAS-NMR spectra of LG30 glass and cement is very close to that value, therefore it can be concluded that it belongs to a small amount of alumina phase that did not melt completely during synthesis.

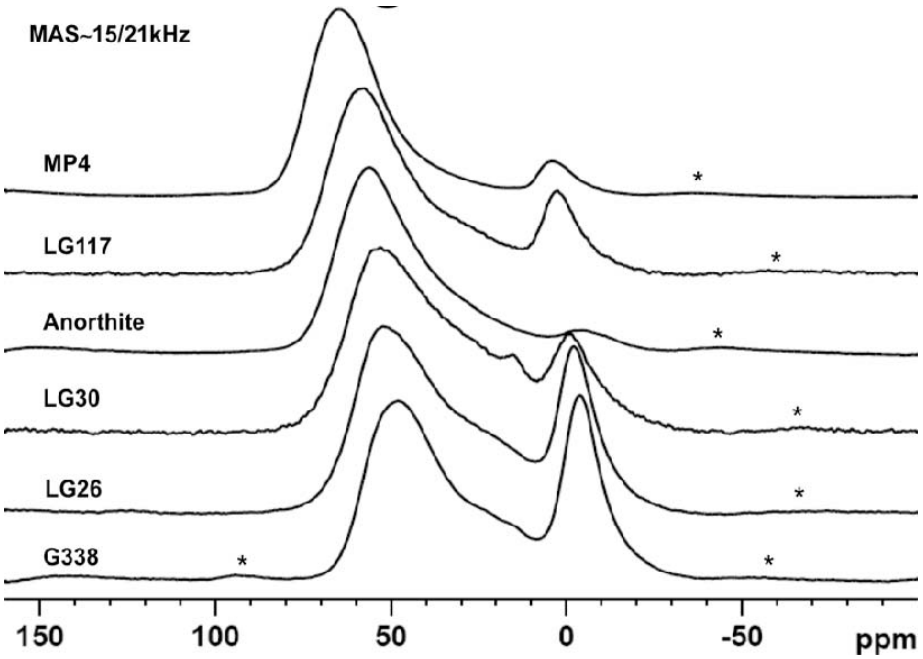

Figure 6.2: 27 Al MAS-NMR Spectra for acetate cements after setting for 24 hours.

After cement formation (Figure 6.2), there is formation of Al(VI) species (3-4ppm) . G338 and LG26 show a marked formation of Al(VI) followed by LG117, LG30 and MP4. Whilst only a small Al(VI) peak is found for anorthite cements.

The spectra for acetate cements are deconvulated and ratio of Al(VI) to Al (IV) is calculated. This ratio is then compared with the theoretical ratio of Al(VI) to Al(IV) calculated from the glass composition for cement formation (Table 6.5).

Table 6.5: Comparison of calculated and deconvulated Al(VI):Al(IV) ratios

	Al(VI):Al(IV)		Glass reacted (%)
	Theoretical	**From NMR**	
LG26	0.21	0.16	75.52
LG30	0.20	0.10	49.16
LG117	0.16	0.08	46.69
Anorthite	0.06	0.07	122.28*
MP4	0.08	0.05	60.71

*The Al(VI) peak is broad in the NMR spectra, hence giving more area under the peak

The calculation is based on the assumption that : 1) a simple acid base reaction between the glass and acetic acid occurs; 2) there is no preferential release of Al cations relative to Ca cations; 3) a complete neutralization occurs in the acid base reaction; 4) for simplification it is assumed that there are no five or six co-ordinated Al present in the glass; and 5) CaF_2 and Al-O-PO_3^{3-} are not involved in setting reaction.

6.5 Discussion:

6.5.1 Selection of Glasses:

The study outlined in Chapter 4 of this thesis showed that hydrolytic stability of acetate cements is based on glass composition. However, the study on the MP4 glass alone was not enough to draw definitive conclusions since it has a high Na content.

To understand the role of fluorine and phosphate in acetate cement formation, glasses from the LG series were used. LG26 contains both fluorine and phosphorus whereas LG117 contains fluorine but no phosphorus and LG30 contained phosphorus but no fluorine. To see if glasses without fluorine and phosphorous could also form hydrolytically stable acetate cements, Anorthite glass was used. This is a simple oxide glass containing silica, alumina and calcium oxide.

Finally, to understand if the sodium content of MP4 was responsible for the hydrolytic in-stability of its acetate cements a sodium containing oxide glass Na-anorthite was melted. This contained approximately same amount of sodium as in MP4.

6.5.2 Discussion of Results:

Comparison of hydrolytic stability with aluminium release suggests that stability of acetate cements depends on aluminium-acetate type system. In Wasson and

Nicholson's study on acetate cements, the authors reported that aluminium acetate is soluble in water and that the insolubility of acetate cements is due to the formation of a silica network. Mehrotra and Bohra (1983) have reported that aluminium acetate is insoluble. This is further confirmed by our results of ICP analysis (Table 5.4). If, for example, Al-acetate was highly soluble in water, the anorthite cement should release 5000 mg/L of aluminium. However, when we look at the results, the release is just 11.81 mg/L which is not even a exceedingly small fraction of this value. This provides further evidence that the Al-acetate complexes are largely insoluble in water.

G338 and LG30 do not form hydrolytically stable cements immediately (Table 5.3). Looking at their aluminium release data at one hour (Table 5.4) it can be noted that there is quite a considerable amount of aluminium release at this time (G338 cement releases 39.41 mg/L of aluminium and LG30 release 20.93 mg/L). This amount is quite high when compared with cements of other glasses which form stable cements at this time. On forming stable cement after 24 hours, the release of aluminium from G338 falls considerably. Although, LG30 also forms a stable cement after 24hours, the release of aluminium from its cement increases to 26 mg/L from 20 mg/L. A possible explanation for this may be that LG30 forms relatively weaker "hydrolytically stable cement" even though the cement is visually hydrolytically stable. This may be attributed to the fact that only 49% of LG30 glass was utilized in the neutralization reaction (Table 5.5) due to which a fair proportion of the glass

remained un reacted. Hence, this aluminium increase could be attributed to the glass particles which did not get neutralized and therefore were not involved in cement formation.

It is interesting to note here that although 60% of MP4 glass was utilized in the reaction but still MP4 failed to produce a stable cement. Furthermore, MP4 has the highest Al:Si ratio (Table 6.6) amongst the glasses used in this experiment. Although, at this high ratio MP4 should be the most reactive and highly stable cement, this does not happen in practical. A look at the composition of MP4 shows that it doesnot follow the Lowenteins rules for glass formulation. This may indicate why this glass behaved different to a typical glass.

Table 5.6: Al:Si Ratio of glasses used in the experiment.

Glass	Al:Si ratio
LG26	1.33
LG30	1.33
LG117	1.33
Anorthite	1.00
Na-Anorthite	0.70
MP4	2.56

Furthermore the hydrolytic stability of Na-anorthite cements confirms that sodium content alone of MP4 was not responsible for its hydrolytic instability.

LG26, LG117 and anorthite showed a relatively lower release of aluminium at one hour. These cements were also hydrolytically stable at this time suggesting that

aluminium played a role in the insolubility of these cements. There is also a further decrease in aluminium release after 24 hours further confirming its role in cement formation. For anorthite cements there is no considerable difference in aluminium release at 1 hour and 24 hours since it's a very reactive glass and almost 100% of the glass was utilized in cement formation (Table 5.5)

Comparison of NMR spectra for acetate cements with that of glasses shows that there is formation of Al(VI) species after cement formation. This is inline with the findings of Stamboulis *et al.* (2006) which observed the same phenomenon with glass poly(alkenoate) cements.

6.6 Conclusions:

Based on the results it can be concluded that the formation of aluminium acetates is one of the factors responsible for the hydrolytic stability of acetic acid cements. Results of ICP clearly show that al-acetates are not highly soluble as previous suggested by Wasson and Nicholson (1993). The reactivity of the glass (dependent on its Al:Si ratio) is also responsible in determining the insolubility of these cements.

Chapter 7

Conclusions and Future work

7.1 Conclusions:

Properties of glass ionomer relating to their fluoride release and setting reactions were studied. The results from all the experiments showed that the formulation of alumino-silicate glasses affects these properties.

Except for AH2, artificial saliva reduced the fluoride release from alumino-silicate glasses. This behaviour of AH2 could not be fully understood, but it suggested that a glass with high sodium and fluorine content will have a higher fluoride release in the oral cavity. Results from LG glasses indicated that replacing calcium with strontium "slightly" increases the fluoride release. This is due to the fact that strontium is a heavier element than calcium and hence there is less of the glass in molar terms and volume fraction for the same P/L ratio (since the P/L ratios were not altered to account for this).

Ultrasound was shown to have a beneficial effect on increasing the release of fluoride from glass ionomer cements, however radiant heat decreases the fluoride release. Results showed that ultrasound not only enhances the initial fluoride release but it also improves the long term fluoride release giving a more sustained release pattern. Once again, AH2 based glass ionomer (Amalgomer) showed highest fluoride release due to its higher fluorine and sodium content.

Studies on acetate cements showed that the theories suggesting a role for silica in glass ionomer maturation and strength development are not valid anymore. Al:Si ratio of the glass controlled the hydrolytic stability of the acetate cements. Glasses with higher Al:Si ratio produced stable cements immediately and continued to do so till 24 hours. However, MP4 did not follow this pattern although it had the highest Al:Si ratio. This is due to the fact that the composition of MP4 does not follow Lowenstein's rules. Release of Aluminium from the cements was analyzed using ICP. The results showed that aluminium release was many orders of magnitude less than what it should be if Al-acetate was completely soluble in water. Further more, its release decreased with time suggesting hydrolytic stability of acetate cements is determined by the formation of aluminium acetate. This clearly casts out on the statement presented by Wasson and Nicholson (1993) that Al-acetates are soluble in water. Although most acetates are soluble in water, basic aluminium acetate is unusual in that it is insoluble. Evidence to support the insolubility of aluminium acetate can be found in the literature (Mehrotra and Bohra, 1983)

7.2 Further Work:

The present work provides better understanding of glass ionomer cements, but nevertheless it brought up more questions for further investigation. In view of this some further work is suggested:

1. The present study only looked at the effect of ultrasound on the release of fluoride from glass ionomer cements. It will be interesting to analyze how the release of other elements such as Al, Si, Ca, P , and Na is effected by ultrasound. This will provide further insight into the effects of ultraound on glass ionomer cements.
2. Although possible mechanisms were discussed, it was still unclear how ultrasound improves the fluoride release. In order to understand if ultrasound effects release from alumino-silicate glasses alone, it is suggested that ultrasound is used to agitate glasses while they are immersed in dilute acetic acid and then look at the release profile with and without ultrasound.
3. ^{29}Si MAS-NMR will provide insight into the setting of acetate cement. It can be used to look at the changes in silica co-speciation and Q structure before and after cement formation.
4. Another suggestion is to use ^{17}O labelled water in cement formation. The Al-O-Si bond is hydrolyzed during cement formation resulting in the formation of ≡Al-OH and ≡ Si-OH that will contain ^{17}O. The condensation re-polymerization of the Si-OH groups to form Si-O-Si can then be followed bi ^{17}O MAS-NMR since they will produce peaks different chemical shifts.

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APPENDIX A

PUBLICATIONS

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The role of glass composition in the behaviour of glass acetic acid and glass lactic acid cements

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Abstract Cements have recently been described, made from glass ionomer glass reacted with acetic and lactic acid instead of polymeric carboxylic acid. From their behaviour a theory relating to a possible secondary setting mechanism of glass ionomer has been adduced. However, only one glass (G338) was used throughout. In this study a much simpler glass ionomer glass (MP4) was compared with G338. This produced very different results. With acetic acid G338 formed cement which became resistant to water over a period of hours, as previously reported, MP4 formed cement which was never stable to water. With lactic acid G338 behaved similarly to G338 with acetic acid, again as reported, but MP4 produced a cement which was completely resistant to water at early exposure and unusually became slightly less resistant if exposure was delayed for 6 h or more. These findings indicate that the theories relating to secondary setting in glass ionomer maturation may need revision.

Introduction

For more than 150 years cements based on acid/base reactions have been used in dentistry. The initial cements used very strong acids (hydrochloric or sulphuric acids) reacted with zinc oxide. In the 1870s these were replaced by the somewhat weaker and less aggressive phosphoric acid to produce the zinc phosphate cement (ZC). In the 1903 the zinc oxide powder was replaced by a glass powder derived from the formulations used in dental porcelain production to produce the dental silicate cement (DSC). In the 1960s the phosphoric acid in ZC was replaced by polyacrylic acid to produce zinc polycarboxylate cement (ZPC). In the 1970s a similar replacement was made in DSC resulting in the glass ionomer cement (GIC). The setting mechanism of all these cements results from cation release from the powder under the acid attack. In the phosphoric acid based cements, as the pH increases with neutralisation of the acid, insoluble species such as zinc phosphate and aluminium phosphate are precipitated. With the polymeric acid based cements it is reported [1] that di- and tri-valent ions such as calcium and aluminium react with the pendant carboxyl groups to form ionic crosslinks between the polymer chains.

Unlike the other three types of cement described above, some GICs show changes in physical properties over prolonged periods (i.e. >24 h). In an attempt to study this change in long-term properties, Wasson and Nicholson [2] made model cements using GIC glass mixed with acetic acid solution (replacing polyacrylic acid). For the first few hours the cement formed was not hydrolytically stable but after 24 h it resisted water.

From this they adduced that some other setting mechanism might also occur since the acetates of all the cations (i.e. Na, Ca, & Al) were readily soluble. More recently Nicholson and Czarnecka have evaluated model cements using lactic acid in place of acetic [3, 4]. The mechanisms discussed involve the production of a complex silicate polymer network. Matsuya et al. [5] reported changes in both infrared and NMR spectra which appeared to support the formation of this secondary silicate network in the GIC

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matrix phase. More recently, De Maeyer et al. [6] using infrared spectroscopy on the glass phase alone found that effect of acid on this component could account for the spectral changes observed. In addition, the particular glass used with both acetic acid and lactic acid [2–4] had certain characteristics that made it unsafe to draw general deductions from results obtained on it alone. Although commercially successful glass ionomer dental restorative cements have been based on this glass (G338) they do not show changes in either compressive or flexural strength at periods >24 h [7, 8]. The composition of G338 is not entirely typical of other GIC glasses as it has high levels of both F and P. Both elements can form anions which have insoluble salts with Ca and Al.

To elucidate the possible role of silicate network formation this studies aims to compare the behaviour of G338 glass with that of MP4 which is a simple oxide glass containing 28%SiO_2; 35%Al_2O_3; 26%CaO; 11%Na_2O. Although cements based on MP4 were developed for orthopaedic splinting where hydrolytic stability was not needed, these cements are known to be perfectly stable in water [9] and have been used in comparisons with dental glass ionomers.

Since this glass contains neither F nor P the potential for insoluble salt formation, apart from silicate is eliminated. The objectives are to evaluate the hydrolytic stability of the reaction products formed from the two glasses each with acetic and lactic acid and to examine the effects of maturation time on all four materials. In addition the infrared spectra will be evaluated to compare with those reported by De Maeyer et al. [6].

Materials and methods

Glasses used were the G338 and MP4. Compositions of both these glasses are shown in Table 1.

For cement formation lactic and acetic acids were used at a concentration of 75% and 45% respectively and a P:L ratio of 3:1 and 4:1 respectively. Optimization studies have shown G338 to produce water stable cements after at least 24 h with these acid concentrations and powder liquid ratios [2, 4]. Cements were prepared by spatulating glass powder and acid solution on a glass slab for not more than 30 s. After this time the mix was packed, under pressure, into circular moulds 1 mm thick and 10 mm in diameter.

Table 1 MP4 and G338 composition

Glass	Al	Ca	F	Na	O	P	Si
G338	16.9	6.6	19.7	6.3	32.5	6.2	11.8
MP4	18.5	18.6	–	8.2	41.6	–	13.1

Table 2 Point system

Score	Features
1/5	Fully intact
2/5	Fully intact with minor surface defects including minor fissures
3/5	Massive fissuring but no disintegration
4/5	Disintegrates into large chunks
5/5	Disintegrates into fine powder

Under this condition, the cements were allowed to set for 1, 2, 3, 6 and 24 h. After these times the cements were dropped into 40 mL of deionised water to assess there hydrolytic stability. Assessment was performed by visual examination based on a point score system (Table 2).

A similar protocol as described above was used for zinc lactate cements prepared by mixing ZnO powder and 75% lactic acid at a P:L ratio of 3:1.

To observe salt formation ATR-FTIR analysis was performed using Perkin Elmer Infrared Spectrometer using a diamond crystal.

Results

G338 glass formed hydrolytically stable cements, with both acetic and lactic acid, when allowed to mature for at least 6 h. Cements immersed in water before this time disintegrated completely turning the solution cloudy and did not retain their disc form. The time taken by the cement to disintegrate was directly proportional to its maturation time. Unlike with acetic acid G338 formed translucent cements with lactic acid however these cements instantly turned chalky white on immersing in water.

The MP4 glass showed different results with lactic acid and with acetic acid. With lactic acid it formed hydrolytically stable cements when allowed to mature for just 1 h. The cements showed no sign of disintegration/solubility except for cracking observed for cements with maturation time of 6 and 24 h. With the acetic acid, MP4 failed to give hydrolytically stable cement throughout the experiment (Table 3; Fig 1). Although the cements had a perfect disc form when taken out from the moulds, but soon after

Table 3 Points scored

	1	2	3	6	24	Total points
G338 (lactic)	4/5	4/5	2/5	2/5	2/5	2.8
MP4 (lactic)	1/5	1/5	1/5	3/5	2/5	1.6
G338 (acetic)	4/5	4/5	1/5	1/5	1/5	2.2
MP4 (acetic)	5/5	5/5	5/5	5/5	5/5	5

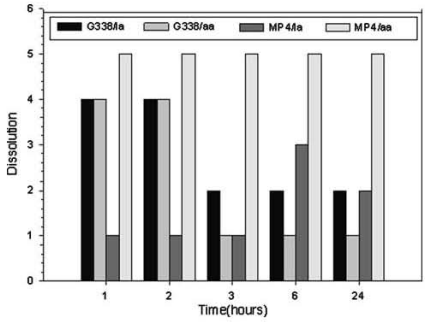

Fig 1 Bar chart depicting dissolution of cements based on the point score system (aa = acetic acid cements; la = lactic acid cements)

immersing in water the cements disintegrated in to fine powder.

To further the solubility/disintegration analysis the immersing solutions were slowly evaporated to dryness in an incubator kept at 37 °C. A residue was observed in all instances except for MP4/lactic acid cements.

Zinc-lactate cement showed hydrolytic stability similar to that of MP4-acetic acid cements.

FTIR-ATR analysis showed rapid salt formation up to 3 h after which no additional salt formation was observed (Fig 2).

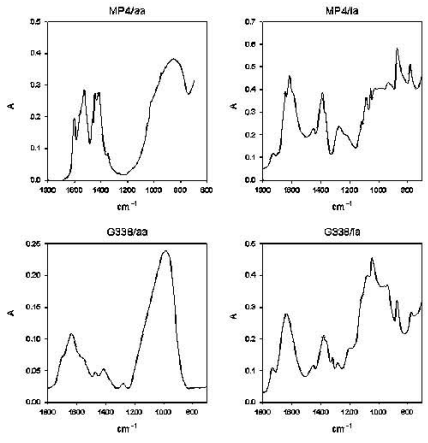

Fig 2 FTIR-ATR scans at 6 h (aa = acetic acid cements; la = lactic acid cements)

Discussion

The results on acetic acid cements demonstrate the hypothesis that maturation of GICs is caused by formation of a silicate network in the polyacid matrix is not viable. MP4 contains the same amount of silica as G338 but does not form an insoluble cement with acetic acid. In contrast, G338 does behave in this way as reported previously by Wasson and Nicholson [2]. Examination of the differences between MP4 and G338 (Table 1) show other elements present in the latter that may account for the formation of hydrolytically stable cements. Both P and F are present in high levels (compared to most GIC glasses). If the initial formation of soluble acetates occurs with acid attack on the glass, as the pH increases these elements may provide anions that could precipitate calcium salts. CaF_2 is very insoluble as are various phosphates such as tricalcium phosphate, calcium pyrophosphate, hydroxylapatite or fluorapatite. The formation of such compounds is analogous to the processes involved in the setting of ZP and DSC materials.

The setting reaction as shown by FTIR traces (Fig. 2) is similar to those found when GICs are examined by this technique.

Understanding the mechanism by which improvements produced by maturation in GICs is potentially of importance since both heat and ultrasound have been used to attempt accelerate this process [7, 8, 10]. Also an understanding of the mechanism may enable GICs with enhanced properties initially to be formulated. However, the maturation of GICs is a complex area. Whereas strength may increase for some materials [11–13] it can also remain unchanged for maturation times beyond 24 h or can increase and then reduce at even longer times [12, 14]. In contrast, resistance to erosion by an impinging jet of lactic acid improves for all GICs tested [15]. Also the resistance to abrasion, under the conditions of three body wear established by ACTA, appears to improve for all GICs tested with maturation times greater than 24 h [16, 17]. Any changes in model cements should therefore be evaluated in respect to the type of property change with maturation observed in the GIC from which the model cement is derived. A number of theories relating to changes in the cement structure have been proposed. Changes in bound to free water have been reported to relate to mechanical property changes in a range of cements including GICs [18, 19]. Changes in the nature of interchain crosslinks have also been suggested to be associated in maturation changes in properties [1, 20]. Although the replacement of Ca ionic crosslinks by Al based ones are discussed no reference is made to the possibility that many of the –COOH groups may first be converted to –COONa. Most of the GIC glasses studied contain this element and it is very mobile.

The replacement of these neutralised but not crosslinking carboxyl groups by Ca or Al (by analogy with the setting mechanism of alginate) may occur in maturation. Another possible maturation mechanism relates to water content. Young suggests [21] that water is required to the extent of 5.6 moles for every mole of acidic group neutralised and that only when additional water is absorbed can full neutralisation occur. Although this appears an interesting theory, improved strength with maturation in oil matches that in water at short times and exceeds it considerably at longer times [11].

De Maeyer et al. [6] reported that G338 treated with acetic acid showed silicate related absorption peaks at 800 and 1,073 cm^{-1} but the former is not shown in our study and the latter would be masked by the carboxylate peaks at 1,000 cm^{-1} (Fig. 2). Our findings agree with the conclusion of De Maeyer et al. that the "silica gel phase is formed as a surface layer on the glass particles and not as a hydrated silicious matrix...." [6].

The behaviour of lactic acid based cements differs from acetic acid based ones. This is not surprising as lactic acid is not as weak an acid as acetic (pKs of 3.86 and 4.76 respectively). Also lactic acid has the possibility forming chelate structures. This difference is clearly indicated in the FTIR spectra which have peaks in areas not shown by acetic acid cements or GICs (see Figs. 2 and 3). In contrast to acetic acid and polyacid in cements the lactic acid concentration used here (the optimum found by Nicholson and Czarnecka [3]) is much higher. Calcium lactate is only moderately soluble [19]. As Nicholson and Czarnecka [3] state in their investigation of lactic acid based cements, "Following our recent work on the interaction of aqueous lactic acid with set glass-ionomers we have become interested in the possibility of forming cements from glass and this acid only..." Although the lactic acid cements have been evaluated as a direct comparison between the behaviour of G338 and MP4 glasses, the lactate cements are plainly not models for GICs in the way that acetic acid [2] or propionic acid [22]ones are; nor were they intended as such. We did, however, note that cement made from zinc polycarboxylate powder and lactic acid was soluble as Nicholson et al reported the acetic acid one to be [3]. Both zinc and magnesium lactates are readily soluble.

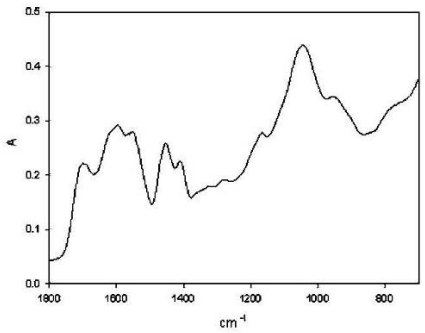

Fig 3 Characteristic FTIR-ATR spectrum of G338 cement with 40% polyacrylic acid

The most interesting aspect of this study is the comparison of MP4 cements with the two different acids. The total failure to form hydrolytically stable cements with acetic acid contrasts with the initial hydrolytic stability of the lactate cements. This latter is a very unusual phenomenon, most dental cements exhibit the reverse behaviour. It would appear that the relatively early exposure to water enhances the cements stability. Possibly the cement may take up water to produce an improved structure; as noted above the lactic acid concentration is very high. The initial hydrolytic stability of the MP4:lactic acid cement suggest that it may have a possible application as a temporary dental cement.

It is concluded that the comparison of the simple GIC glass MP4 with G338 enables some of the theories on GIC maturation to be eliminated. The behaviour the novel MP4 lactic acid cement may provide a mechanism for improving dental cements.

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Kinetics of fluoride ion release from dental restorative glass ionomer cements: the influence of ultrasound, radiant heat and glass composition

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Abstract To compare the effect of ultrasonic setting with self curing on fluoride release from conventional and experimental dental glass ionomer cements. To compare hand mixed and capsule mixing and the effect of replacing some of the reactive glass with zirconia. In a novel material which advocated using radiant heat to cure it, to compare the effect of this with ultrasound. To evaluate the effect of ultrasound on a glass ionomer with fluoride in the water but not in the glass. 10 samples of each cement were ultrasonically set for 55 s; 10 controls self cured for 6 min. Each was placed in 10 ml of deionised water which was changed at 1, 3, 7, 14, 21, 28 days. The solution fluoride content was measured using a selective ion electrode. All ultrasound samples released more fluoride than the controls. Release patterns were similar; after a few days, cumulative fluoride was linear with respect to $t^{1/2}$. Slope and intercept of linear regression plots increased with ultrasound. With radiant heat the cement released less fluoride than controls. The effect of ultrasound on cement with F in water increased only slope not intercept. Zirconia addition enhances fluoride release although the cement fluorine content is reduced. Comparison of capsule and hand mixing showed no consistent effect on fluoride release. Ultrasound enhances fluoride release from GICs. As heat has an opposite effect the heat from ultrasound is not its only action. The lesser effect on cement with fluoride only in the water indicates that of ultrasound enhances fluoride release from glass.

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1 Introduction

Glass ionomer cements (GICs) were first developed in the 1960s by Wilson [1]. They are currently used as one of the alternatives to amalgam restoratives as a tooth coloured restorative cement, as they are aesthetically better than metal restorations and they bond directly to tooth tissue. They may also be used as a dental luting cement having several advantages compared to zinc phosphate cements which had been used for crown cementation previously. They have low setting exotherm and therefore they will not cause thermal damage to the pulp tissue. They also can release fluoride, which provides anticarcinogenic effects. They have good biocompatibility and chemically bond to enamel and dentine. These properties make glass ionomer cements used quite extensively in dental applications [2].

Early water/saliva contamination leading to a softened or disrupted matrix on the cement surface is a distinct problem [2]. The soft surface reduces the wear properties of the cement when in the mouth. In addition to improvements to the GICs, studies are being carried out into methods set acceleration to address this problem.

The methods that have been investigated are the application of ultrasound and heat to accelerate the setting [3–6]. This has been investigated using an ultrasonic scalar device. The results of these studies indicate that application of ultrasonic to GICs accelerates the rate of set of these cements. They showed improvements in the physical properties of the GIC. An increased rate of set as indicated by hardness of a GIC Fuji IX (FIX) was observed using a nano indentation technique [3]. A further study carried out

by Kleverlaan et al. [4] showed an increase in the hardness properties and compressive strength of FIX Fast and Ketac Molar (KM) cements. However they suggested that for this improvement in the mechanical properties was 'The setting of GICs may partially be explained by the heat effect.'

Both studies suggest that the ultrasonic vibration directly enhances the setting reaction of the GIC. The vibration enhances intimate contact of the glass particles with the polyacid solution thus accelerating the reaction. The compaction of the particles leads to enhanced mechanical properties and has the potential for void reduction. Due to the acceleration of the setting times for GICs, this makes the cements less susceptible to water uptake, therefore reducing the development of a softened matrix on exposure to water.

More recently, Rushe and Towler [7] demonstrated the influence of ultrasound on the fluoride release of commercial and experimental glass ionomer luting cements.

This study is designed to investigate the effect of ultrasonic setting (UC) on fluoride release from a range of commercial GICs by comparing that from standard set (SC) samples of the same GICs. A further aim of this study is to compare the fluoride release from capsulated and hand mixed version of the same GICs. Additionally the fluoride release of a glass ionomer containing zirconia as a reinforcing and radiopacifying filler will be compared with the product in a zirconia-free version.

The manufacturers of another commercial Glass Carbomer (GC) product advocate the use of the radiant heat (RC) from a commercial dental curing light to produce the accelerated set created by ultrasound and the effects of the two types of radiation on fluoride release will be compared.

Ultrasound may influence the fluoride release as a result of changes in the glass polyacid reaction or diffusion rate of fluoride through the cement. To investigate this, a GIC with a fluoride free glass with NaF added to the water component will be studied for the effect of ultrasound on fluoride release rate. Cumulative release will be studied over a period of 28 days to enable both initial "burst" and "steady state" release to be evaluated.

Analysis of the elemental composition of all the glasses used in the GICs in the study was carried out by an external laboratory.

2 Materials and methods

There were two conventional GICs used GC FIX (GC Dental, Japan) and KM [3M Espe, Germany] glass compositions shown in Table 1. These were in capsules (CM) and as powder and liquid form for hand mixing (HM). An fluoride free experimental glass LG30 (Limerick University), composition shown in Tables 2, 3. Additionally a commercial GIC Amalgomer (AM, Advanced Healthcare Ltd, UK) which consists of AH2 glass powder and polyacrylicacid homopolymer was available in capsules, powder water presentation for HM and with 19.7% zirconia ceramic particles as radiopacifying secondary ceramic filler particles (AMC). GC (Glass Carbomer, Holland) was available in capsule form only. It contains fluorapatite as a secondary filler and the reactive glass has been treated with dialkyl siloxanes described in European Patent 20040748628. The experimental glass ionomer was made from fluoride free experimental glass LG30 (Limerick University) mixed with polyacrylic acid powder provided by Advanced Healthcare molecular weight 50 kD. Samples were mixed with either water or 2% NaF solution. Details of the glass compositions (analysis by Ceram Research) are given in Table 1.

10 specimens of each cement were prepared for each setting process. All sample preparation was carried out at room temperature. HM was performed using a spatula and paper mixing pad. After activation the capsule was placed in a rotating mixer, Rotomix for 10 s as per manufacturer's instructions. The mixed capsule was then loaded into the gun. A polyethylene mould of dimensions 3 mm diameter and 2 mm thick (Fig. 1) was placed on a sheet of acetate and the mixed cement was injected into the mould, then covered with acetate sheet. The acetate sheets were used to obtain a flat surface area of each specimen, therefore

Table 1 Weight percentage composition of GIC glasses

Element	Si	Al	Ca	Na	F	P	Sr	La
FIX	13.7	17.9	0	1.0	10.2	2.2	19.9	0
KM	12.4	15.0	10.1	1.7	13.3	2.0	0	17.6
LG30	14.6	18.1	13.9	0.05	0.04	6.4	<0.01	<0.01
AH2	18.7	15.8	7.1	5.5	12.9	1.6	0	0
GC	20.0	14.1	2.1	1.9	9.0	2.5	13.6	0

Table 2 Slope (m) and the intercept (C) for the fluoride release of GC over 28 days

Material	m	C	R^2
GC/SC	0.129	0.064	0.998
GC/US	0.345	0.101	0.997
GC/RH	0.102	0.036	0.993

Table 3 Effect of setting methods on slope (m) and intercept (C) of GC

	Effect of US vs. SC	Effect of HC vs. SC
On m	×2.67	×0.79
On C	×1.58	×0.56

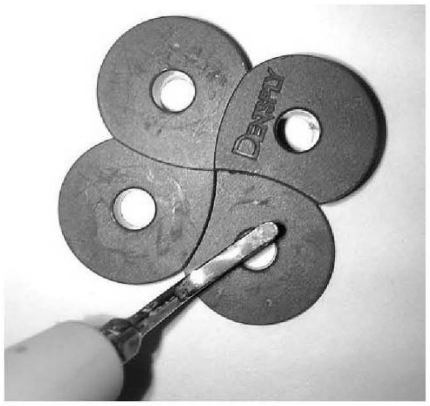

Fig. 1 Application of ultrasound to cement

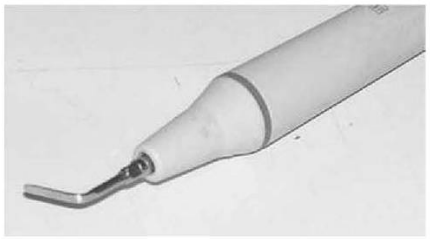

Fig. 2 Tip of ultrasonic scaler

ensuring that the dimensions remained the same. The specimens were then left for 6 min to SC.

A further set of 10 specimens were prepared and set using a ultrasonic hand piece with a flat tip scaler (Fig. 2), the ultrasound was applied to the cement that was employed using EMS Piezon Master 400 Dental Scaler operating at a maximum frequency of 45 kHz that was set on the maximum power setting. The flat tip of the scaler was moved continuously on the surface in a uniform manner over the acetate sheet where the ultrasonic waves penetrated through into the cement for 55 s as optimized previously [8]. A near uniform US field is found at least to a depth of 4 mm [9].

All samples were placed in 15 ml centrifuge tubes and left to equilibrate for 24 h, before adding 10 ml of deionised water and storing them in an incubator at 37°C. The deionised water was changed at intervals of 1, 3, 7, 14, 21, 28 days. The solutions were then tested for fluoride content using an Orion Ionplus Fluoride Electrode.

3 Results

The plots of the cumulative fluoride release versus $t^{1/2}$ the commercial GICs all show a very strong positive correlation with correlation with $t^{1/2}$. The GC results are shown in Fig. 1 demonstrating the effects of UC and RC compared to SC. The results for capsulated FIX are shown in Fig. 2 showing the results for a conventional GIC with similar fluoride content glass with novel GC. The results in Fig. 3 show the effect of ultrasound on LG30 both with and without NaF addition. In all cases the cumulative fluoride release results show very strong correlations with $t^{1/2}$. Therefore the values of R^2, m, and C for the equations $[F] = m\,t^{1/2} + C$ are shown in Tables 2–13. Together with the effects of various changes in m and C produced by the various changes in experimental variables (type of cure regime, method of mixing, and effect ceramic filler addition) below the relevant tables (Figs. 4, 5).

4 Discussion

Results for all restorative commercial GICs show ultrasound to enhance F-release. This is in line with Rusche and Towler's findings [7] for luting GICs. In both studies the release rate is linear with respect to $t^{1/2}$ indicating a diffusion controlled mechanism. In no instance is there any indication that the UC enhancement falls off with time. In this study good linearity is observed up to 28 days and in Rushe and Towler's case 90 days. In this study their results re-plotted against $t^{1/2}$ show that both m and C of the best fit equation: $[F] = m\,t^{1/2} + C$ are increased for the commercial luting cements Ketac Cem and Fuji I. Our study of the equivalent restoratives KM and FIX show the same effect but m and C are generally increased much more in this study. Their increases for m were $\times 1.4$ for Fuji I and $\times 1.22$ for Ketac Cem and $\times 2.2$ and 2.0 for C. The lesser effect may reflect either the lower glass content of the luting cements or the longer duration of ultrasonic irradiation in this study. This was selected as optimal from a study in the conversion of carboxylic acid groups to carboxylate salt groups using ATR-FTIR [8]. The increase in both m and C suggests that more fluoride is available for release rather than increased diffusion as the major effect. Rushe and Towler discussed possible causes of enhanced fluoride release and suggest the most likely explanation is enhanced reaction due to greater glass surface area available for reaction. They cite reduction in mean particle size due to cavitation [10]. Their general conclusion is in line with our findings for m and C and those of Talal et al. [8] on carboxylate conversion. Further evidence of this is provided by the results on LG30 + NaF. The average effect of UC on m in this study is to increase it by 159% ($\times 2.59$) and

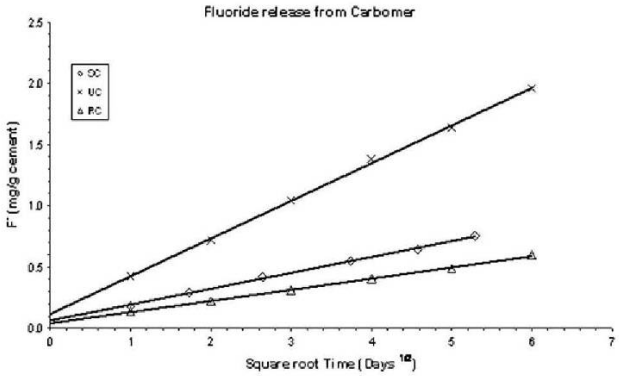

Fig. 3 Fluoride release from Glass Carbomer

Table 4 Slope (m) and the intercept (C) for the fluoride release of both FIX and KM over 28 days

Material	M	C	R^2
KMHMSC	0.0593	0.112	0.926
KMHMUC	0.122	0.427	0.889
KMCMSC	0.110	0.093	0.969
KMCMUC	0.195	0.266	0.961
FIXHMSC	0.057	0.202	0.948
FIXHMUC	0.139	0.281	0.965
FIXCMSC	0.083	0.112	0.976
FIXCMUC	0.316	0.428	0.973

Table 5 Effect of UC versus SC on m and C of KM and FIX

	Material	HM	CM
On m	KM	×2.06	×1.77
	FIX	×2.44	×3.81
On C	KM	×3.81	×2.86
	FIX	×1.39	×1.52

Table 6 Effect of hand mix versus cap mix on m and C of KM and FIX

	Material	SC	UC
On m	KM	×1.85	×1.66
	FIX	×1.46	×2.27
On C	KM	×0.83	×0.63
	FIX	×0.55	×1.52

Table 7 Slope (m) and the intercept (C) for fluoride release of both HM and CM Amalgomer and Amalgomer CR over 28 days

Material	m	C	R^2
AMHMSC	0.161	0.080	0.998
AMHMUC	0.343	0.238	0.991
AMCMSC	0.125	0.076	0.999
AMCMUC	0.378	0.291	0.972
AMCCMSC	0.183	0.549	0.893
AMCMUC	0.510	0.895	0.961

Table 8 Effect of US versus SC on AM HM and CM

	AM/HM	AM/CM	AMCR/CM
On m	×2.13	×3.02	×2.79
On C	×2.98	×3.83	×1.08

Table 9 Effect of CM versus HM of AM

	SC	UC
On m	×0.78	×1.10
On C	×0.95	×1.22

Table 10 Effect of ceramic addition, AMCCM versus AMCM

	SC	UC
On m	×1.46	×1.35
On C	×7.22	×3.08

C by 167% (×2.67) compared to SC for all commercial materials in this study (see Tables 2–10). The Rushe and Towler values [7] increase 30 and 111%, respectively. In contrast, for LG30 + NaF m increases by only 33% and C decrease by 2%. (see Table 5). It therefore seems likely that UC has a small effect on diffusion from the cement

Table 11 Effect of US on LG30 with and without NaF (in the water)

Material	M	C	R^2
LG30SC	0.212	0.812	0.908
LG30UC	0.812	−0.0701	0.962
LG30 + NaFSC	3.294	4.578	0.976
LG30 + NaFUC	4.373	4.492	0.991

The results here are in microg F as contrasted to other tables in mgF

Table 12 Effect of US versus SC on LG30 and LG30 + NaF

	LG30	LG30 + NaF
On m	×3.83	×1.33
On C	× ~0.00	× 0.98

Table 13 Effect of NaF addition

	SC	UC
On m	×15.54	×5.39
On C	×5.6	"v. large"

matrix into the surrounding water and a larger effect on fluoride ion release into the matrix from the glass. Additional evidence in support of this hypothesis is provided by the results from the LG30 controls. Although, the formulation is designed to be fluoride free impurity levels of fluoride were found on analysis by Williams et al. [11] (as shown in Table 1). The increase in m produced by UC is much higher than that produced by UC on the formulation with NaF. (The effect of UC on C did not change.) It therefore seems that most effect of UC is on fluoride ion release from glass into the polyacid matrix although release may be into the depleted layer around glass particles from which release occurs more easily into water than from the non-acid-treated particles [12, 13].

The effect of capsule mixing on fluoride release is very variable. Two of the three materials show increased m for capsule mixed SC compared to hand mixed, whereas for UC all three show increases. All three comparisons show reduced values of C for SC whereas two of them show increases for UC (see Tables 4–10).The effect of method of mixing on F-release has not been subjected to much study, only a poster presentation at BSDR 2005 dealt with effect of porosity on fluoride release and uptake [14] and Verbeek et al. [15] showed considerable increase in both short and longer term release for capsule mixing but for only one material.

Looking at the interaction between method of mixing and effect of UC for FIX and Amalgomer the UC effect is enhanced for both m and C. For KM it is reduced slightly for m but by 24% for C. In a previous study Jones et al. [16] have indicated higher levels of porosity in FIX than in KM. This may therefore suggest that porosity reduction may be a factor influencing the difference observed.

The results for glass GC when self cured are very similar to the other GICs tested in this study. The siloxane incorporation into the material referred to in the manufacturer's patent does not produce any marked difference in the type of [F] v $t^{½}$ plot produced. The level of enhancement by UC of m and C is also similar. The interesting feature of this product is the manufacturer's advocacy of the use of a dental curing light with appreciable radiant heat output to accelerate the set. Using the curing light recommended for their specified duration produced reductions in m and C compared to SC. These results are the only ones comparing

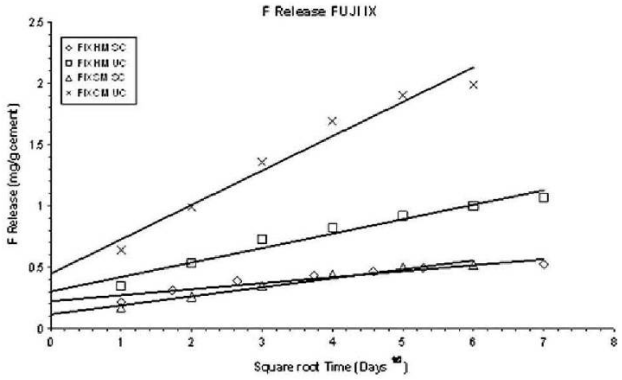

Fig. 4 Fluoride release from capsule and hand mixed Fuji IX

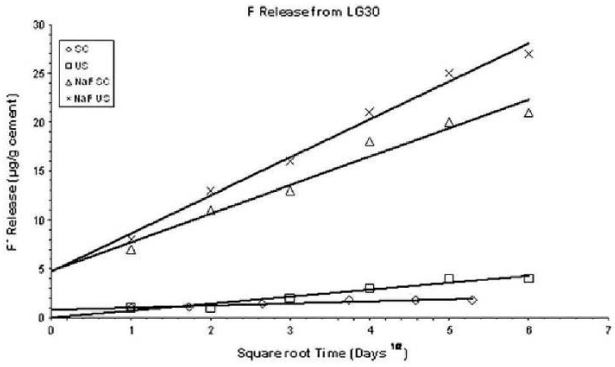

Fig. 5 Fluoride release from LG30 cement with water or 2% NaF solution

the effect of heat and ultrasound on F-release. The effects on compressive strength are reportedly similar on other GICs, i.e. both produce enhancement compared to SC [4]. Examining the conversion of the ratio of carboxylic acid to carboxylate peaks (as described in Talal et al. [8]) shows 187% increase for UC compared 157% for RH after 10 min. After 60 min they are similar UC 187%, RH 195% and SC is 192%. Though not a direct comparison Rushe and Towler [7] showed UC enhanced fluoride release whereas Woolford and Grieve [17] showed reducing levels with increasing duration of infrared radiation. This comparison therefore provides direct evidence that UC produces effects other than those arising from the heat that is generated in its application to GIC.

The results of Amalgomer and Amalgomer CR provide the direct comparison between a GIC and a similar material with a secondary filler 19.7% ZrO. Although the secondary filler is fluoride free and replaces an appreciable proportion of the fluoride containing glass the effect on fluoride release is higher both for SC and UC. Particularly surprising is the relative effects on m and C (see Table 10). The larger effect is on C suggests that the initial "wash out" is greater. Previous studies with GICs having secondary fillers have been of GICs having very large weight percentages of silver or silver tin alloy [18] and showed reduced fluoride release. GC contains fluorapatite as secondary filler but no material without this present was available for a comparison to be made.

Since the composition of all the commercial GIC glasses had been determined (Table 1) it was possible to evaluate the effects of Na and F content on the fluoride release both as m giving a measure of diffusion controlled continuing release and C as a measure of initial "burst" or "washout" behaviour. NOTE this was not a primary objective of this study and the effects would be confounded by other factors such as method of mixing, presence or absence of secondary filler, and different polyacids. The fluoride contents also had a more limited range (9.0–13.3%) as contrasted to (1.0–5.3%) for Na. (The results for LG30 were excluded since it had a negligible F content and would therefore have had effectively no fluoride release thus skewing the statistics.) Table 14 shows the correlation coefficients (in the form of R^2) from linear regression analysis. All values of R were positive but only the effects on m and C of Na for SC samples were statistically significant. The correlations were always weaker for UC than for SC. The absence of positive link between fluoride content (in the range used in commercial dental GICs) and fluoride release has been reported previously [19]. The correlation for C and Na was particularly strong. This is in line with findings with glasses where only the Na content of the glass was varied [20]. Although values of m and C were not determined in that study, the initial release over 64 h increased much more than the subsequent cumulative release from 64 h to 12 weeks. The release relative to the Na-free glass rose from 15% for 0.3% Na to 130% for 1.2% Na for initial release as contrasted with −12% to +39% for subsequent cumulative release.

Further work should include evaluation of the other elements released from the GICs SC, UC, and RC.

Table 14 Effect of F and Na content of glass on F-release (values of R^2 from linear correlations with m and C)

Cure type	Element	M	C
SC	Na	0.66 ($P = 0.05$)	0.88 ($P = 0.01$)
UC	Na	0.53 ($P > 0.05$)	0.12 ($P > 0.05$)
SC	F	0.07 ($P > 0.05$)	0.24 ($P > 0.05$)
UC	F	0.001 ($P > 0.05$)	0.14 ($P > 0.05$)

Evaluation of effect on fluoride ion uptake of these three setting conditions and effect of setting conditions on the susceptibility of GIC to disruption (roughening) by neutral fluoride solution.

5 Conclusions

Ultrasound accelerated setting enhances fluoride release from GICs. Heat accelerated setting has an opposite effect. This confirms that heat generated by UC is not its only effect where the fluoride content of the GIC is present in the water of the GIC rather than in the glass the effect of UC is much less indicating that UC acts on F-containing GICs to enhance fluoride release from the glass component. The effect of HM compared to capsule mixing on fluoride release is not in a consistent direction. The presence of an inert Zirconia secondary filler enhances fluoride release although the fluoride content is reduced. The Na content of the glass enhances initial fluoride release more than subsequent release rate.

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Polyalkenoate Cements Based on Simple $CaO-Al_2O_3-SiO_2$ Glasses

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Abstract

Glass polyalkenoate cements are formed from reacting $CaO-Al_2O_3-SiO_2$ glasses with aqueous poly(acrylic acid). The polyacid degrades the glass releasing Al^{3+} and Ca^{2+} cations, which then ionically crosslink the polyacid chains resulting in the formation of a hard ceramic like cement.

Five glasses were investigated based on $(1-X)CaO(1-X)Al_2O_3(2+2X)SiO_2$ with varying Al:Si ratios. The cement properties were found to be highly dependant on the Al:Si ratio of the glass. The setting and working times of the cements decreased with increasing Al:Si ratio, whilst the compressive strength increased. Infra red spectroscopy showed increased setting rates with increasing Al:Si ratio.

^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) showed that the ratio of Al(IVI:Al(VI) in the cements increased with the Al:Si ratio of glass. In summary the reactivity of the glasses increased with their Al:Si ratios consistent with acid hydrolysis of Al-O-Si bonds being the rate controlling process in these cements

1.0 Introduction

Polyalkenoate cements are normally formed by reacting a specially synthesised fluoro-alumino-silicate glass with a polycarboxylic acid, such as poly(acrylic acid) [1,2]. The polyacid hydrolyses Al-O-Si bonds in the glass network (Figure 1a) releasing Al^{3+} and Ca^{2+} cations which are chelated by the carboxylic acid groups and serve to ionically crosslink the poly(carboxylic acid) chains resulting in a hard ceramic like cement. The setting reaction is shown schematically in Figure 1b

Polyalkenoate cements are known as glass ionomer cements and are widely used in dentistry for fissure sealants, tooth fillings and adhesives [3]. They are rapid setting cements, setting typically in 5 minutes or less. They exhibit very high compressive strengths, often greater than 200MPa and flexural strengths greater than 40 MPa, after ageing for 24 hours. They bond chemically to the tooth mineral, via ion chelation by carboxylic acid groups of the polymer which eliminates the need for undercutting to keep the cement in place.

They set readily even in the presence of water and do not expand or contract signficantly on setting.

The dental versions are made with specially synthesised fluorine containing glasses [4]. Fluorine is incorporated into the glass for two main reasons:

i) to reduce the refractive index of the glass to match the polysalt matrix in order to have a translucent cement with good aesthetic appearance.

ii) To provide fluoride ions for preventing secondary caries or tooth decay.

Polyalkenoate cements are potentially attractive materials for the building industry if inexpensive fluorine free glasses could be used.

Applications include rapid repair materials, where the fast setting characteristics and potential chemical adhesion to Portland cement via calcium ion chelation are attractive features.

They also have potential for moulded cement and concrete products where their ease of moulding, rapid setting and fast strength development are attractive features. They would be very suitable for applications like roof tiles where their high strength and good strength to weight ratio are attractive features. These cements can also be thermally cured for example by autoclaving and could also be fibre reinforced using conventional E glass fibres, since their pH remains on the acid side of neutral. They have negligible porosity and should have excellent freeze-thaw resistance

The reactivity of the glasses used is thought to depend on two factors:

i) the number of acid hydrolysable bonds in the glass and in particular the ratio of Al:Si

ii) the degree of network disruption and on the network connectivity defined here as average number of bridging oxygens per Si and Al in the glass.

Of these two factors the Al:Si ratio is thought to be the dominant parameter.

There are two options for forming inexpensive glass polyalkenoate cements. The first is to use waste glasses from coal combustion processes. One option here is to use slags from commercial coal gasification plants [5,6]. Here coal is mixed with lime stone and combusted in a reactor to produce methane, carbon monoxide and a waste calcium alumino-silicate glass, containing small amounts of magnesia, alkali metals and iron. Another option is to use fly ashes from coal combustion processes based on lignite coals that are rich in CaO.

The disadvantage of using waste materials is the variability in the composition of the final material and that often these materials have far from optimum compositions

The second option is to use specially synthesised glasses, which is a more expensive option, however it may be possible to use a combination of both approaches for example by blending a specially synthesised reactive glass with a less reactive waste glass.

This paper investigates simple $CaO\text{-}Al_2O_3\text{-}SiO_2$ glasses for polyalkenoate cement formation and in particular the Al:Si ratio on the properties of the glass and the resulting cements.

The objectives are to investigate the feasibility of using specially synthesised glasses and also to provide selection criteria for the identification of suitable gasifier slag compositions.

A secondary objective is that new insights into the setting chemistry of glass polyalkenoate may be obtained by investigating simpler $CaO\text{-}Al_2O_3\text{-}SiO_2$ glass compositions than the more complicated fluorine and phosphate containing compositions normally used to form the commercial dental and medical materials.

The complex fluoro-alumino-silicate glasses and cements have been extensively investigated previously [4, 7-16]. Compositions based on gasifiers slags have also been investigated [5,6] however there is only one limited study of simple $CaO\text{-}Al_2O_3\text{-}SiO_2$ glasses [16].

2.0 Experimental

2.1 Glass Design

The glasses were all based on a stoichiometric anorthite glass $CaO\text{-}Al_2O_3\text{-}2SiO_2$ and form a series based on $(1\text{-}X)CaO(1\text{-}X)Al_2O_3(2+2X)SiO_2$.when X=0 this corresponds the anorthite composition ($CaOAl_2O_32SiO_2$). In these glasses there is just enough CaO to charge balance charge deficient AlO_4^- tetrahedra and the Al:Si ratio is varied and is one or less. All the glasses have a network connectivity of 4.00.

These glasses have sufficient Ca^{2+} to charge balance the charge deficient ALO_4^- tetrahedra and have an Al:Si ratio less than one in order to meet Lowenstein's Al

avoidance principle and prevent the aluminium taking up coordination states greater than four [17].

2.2 Glass Synthesis

Glasses were synthesised by mixing Calcium carbonate ($CaCO_3$), alumina (Al_2O_3) and silicon dioxide (SiO_2). The compositions of the glasses are given in Table 1. All the glasses were melted in 300ml a platinum-rhodium crucible at a temperature of 1550-1600^oC for 1.5 Hrs. The resulting melt was shock quenched into deionized water to produce a granular glass frit, which was then dried at 125^oC. Then 100g portions were ground in a hardened steel puck mill for two periods of 7 mins. The resulting glass powder was the sieved through a 45 micron sieve for 30 mins and the powder <45 microns used for cement formation. The grinding and sieving processes were standardised to try and avoid changes in glass particle size.

2.3 Glass Powder Characterisation

The <45 micron powder was characterised by X-ray powder diffraction The particle size of the powders was characterised by laser light scattering using a Malvern particle size analyser High temperature differential scanning calorimetry of the <45 micron powder was performed to determine the glass transition temperature of the glass and the peak crystallisation temperatures. The Tg was measured since very reactive glasses can be annealed at Tg to reduce their reactivity.

2.4 Cement formation

The glass powder (2.5g) was mixed with poly(acrylic acid) (0.5g) and this was then mixed with 0.5ml of distilled water containing 10% m/m (+) tartaric acid. Tartaric acid is used in commerciall dental cement formulations to extend the working time of the cement and shorten the setting time [18-20].

The working and setting times of the cement pastes were determined using an Oscillating Rheometer. This apparatus consists of two plates, one of the plates is fixed whilst the other is oscillated by means of an eccentrically driven spring. The amplitude of the oscillation is measured and plotted against time on a chart recorder. The apparatus is shown schematically in Figure 2a and a typical rheogram in Figure 2b. The time for the amplitude to reduce to 95% of its value was taken as the working time of the cement paste and the time to for the amplitude to reduce to 5% was taken as the setting time. Measurements were performed at 21 ± 3^{o}C. Three measurements were performed for each cement formulation.

2.5 Compression Test

The compression tests were performed on cement cylinders 4.0mm in diameter by 6.0 mm in height. The testing procedure was based on the ISO standard" ISO7489 : 1986 Dental Glass Polyalkenoate Cements" [21] An Instron tensometer (Instron High Wycombe Bucks UK) was used for the test at a crosshead displacement rate of 1mm.

min^{-1}. The test was carried out on 8 samples and the compressive strength calculated according to:

$$\sigma_c = F/\pi r^2$$

Where: F is the maximum force and r is the radius of the cylinder.

2.6 Solid State ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS-NMR)

^{27}Al MAS-NMR was carried out on the glass powders and the set cements after 1 and 28 days . In the case of cements the cements the reaction was stopped by immersing the cement in liquid nitrogen followed by dehydration in ethanol using the method first developed by Matsuya et al. [22].

2.7 Fourier Transform Infra Red FTIR) Spectroscopy

The aborbance ratio for the carboxylate group at 1550cm^{-1} to the carboxyl group at 1700cm^{-1}.was determined by ATR-FTIR for the first hour of setting.

The absorbance ratio at 1700/150cm^{-1} corresponding to the free carboxylic acid group to carboxylate group was plotted against time and the slope calculated. The slopes give a measure of the rate of setting.of the cement. The procedure follows closely the approach used by Young [23]

3.0 Results and Discussion

All the glasses gave optically clear glass frits that were amorphous and free from any obvious crystalline inclusions by X-ray powder diffraction.

Table 2 gives the results of the particle size analysis. All the glasses have a very similar particle size distribution. HTM1 had a slightly smaller particle size.

Figure 3 shows the ^{27}Al MAS-NMR spectra of the glasses. The peak position is between 50 and 60ppm and the dominant aluminium species is A(IV). There is no significant proportion of Al(VI) in the glasses that would be observed at 5 to -5ppm. The peak position of the chemical shift is plotted against Al:SI ratio in Figure 4 and it moves progressively to lower chemical shift with decreasing Al:Si ratio or X moving from 57.5pppm to 52.2ppm on decreasing X from 25 to 14. This is consistent with a previous study by Neuville et al. [24] The absence of Al(VI) contrasts with the more complicated fluorine glasses investigated previously. The presence of Al(VI) in the glass prior to cement formation complicates the quantitative analysis of the cement spectra.

Typical differential scanning calorimetry (DSC) traces are shown in Figure 5 and the values for the glass transition temperature and peak crystallisation temperature plotted in Figure 6 The Tg changes only very slightly with Al:Si ratio, whilst the crystallisation temperature increases and its amplitude decreases with decreasing

Al:Si ratio and as the stoichiometry of the glass moves further and further away form the stoichiometry of anorthite, which was the crystalline phase that formed.

The working times and setting times of the cement pastes are plotted against the Al:Si ratio of the glass in Figure 7.. Both the working times and the setting times decreased with increasing Al:Si ratio of the glass. This result was expected as there are more Al-O-Si bonds for acid hydrolyse which would be expected to result in faster release of Ca^{2+} and Al^{3+} cations and more rapid ionic crosslinking of the pollycarboxylic acid chains A previous study by Wilson et al. [16] showed no correlation of setting and working times with the Al:Si ratio however no information was given on the particle size distribution of the glasses and particle size and surface area would be expected to have a dramatic influence on the reactivity of the glasses and their working and setting times. A study by Griffin and Hill [12] investigating more complex fluoro-aluminosilicate glasses containing phosphate also found Al;Si ratio to not be important, but the results here are thought to be a consequence of the formation of Al-O-P bonds in the glass. The decrease in the setting and working times found in the present study were not linear with increasing Al:Si ratio but decreased more rapidly with an increase in Al:Si ratio from 0.39 to 0.56 and then less rapidly from 0.56 to 1.00 .

Figure 8 shows the compressive strength for cements plotted against the Al:Si ratio. The compressive strength increases with increasing Al:Si ratio, The compressive strength values from Wilson et al [16] are plotted alongside the current results. These

cements had a slightly higher glass to liquid ratio 3:1.than that investigated in the present study of 2.5:1. Wilson *et al.* also found an increase in compressive strength with Al:Si ratio. The values for the compressive strength in the present study reach a plateau or fall at high Al:Si ratio. This is thought to be a result of the high reactivity of the glasses and especially with the anorthite stoichiometry glass that has the highest Al:Si ratio. and a consequently shorter working time that makes obtaining a homogenous cement paste difficult. As a result the compressive test cylinders of this cement had a much higher proportion of defects and consequently a lower compressive strength.

It was noticed that the 28-day aged compression samples for HMT5 had deformed slightly and swollen and increased their dimensions from 4.0mm to an average diameter of 4.5mm. and there was a pronounced tendency for the surface to flake off on contact. Not surprisingly, this was reflected in the lowest compressive strengths of all the compositions. Samples from HMT4 also exhibited some slight swelling.

In general the compressive strength increased with increasing ageing time. The increase in compressive strength has been attributed to increased ionic cross-linking of the poly(acrylic acid) chains with time [26,27]

Figure 9 plots the rate of change of the Absorbance Ratio of the carboxylate group at 1550cm^{-1} to the carboxyl group at 1700cm^{-1} which we term the Rate of Set against the Al:Si ratio of the glass. The Rate of Set increases with increasing Al:Si ratio. This indicates that the higher the Al:Si ratio of the glass the faster the setting reaction and

this agrees with the shorter working and setting times and increasing compressive strength with increasing Al:Si The HTM1 glass with the slightly smaller particle size distribution has a faster Rate of Set than expected, though this was not manifested in the measured setting and working times.

Figure 8 shows ^{27}Al MAS-NMR spectra for the HTM2 glass and and the respective cements at 1 and 28 days. The formation of Al(VI) can be clearly seen in the cements with a chemical shift close to zero ppm. The proportion of Al(VI) increases with time, which has been observed in previous studies with more complex fluorine containing glasses [2, 22, 28-30]. In the case of glasses with a low Al:Si ratio the Al(VI) peak grows significantly in intensity between 1 and 28 days. In contrast there is relatively little increase in the proportion of Al(VI) for cements based on glasses with high Al:Si ratios.

There is a weak shoulder at about 4ppm which is more clearly seen in some of the cements and from previous studies on commercial dental cements [30] it is assigned to an Al (VI) species associated with the (+) tartaric acid. added as a rheological modifier.

Table 3 gives the integrated peak intensities for Al(IV) and Al(V) and Al(VI) plus the ratio of Al(VI)/((Al(IV)+Al(V)), the predicted Al(VI)/((AL(IV)+Al(V ratio assuming complete neutralisation and the calculated percentage of the reaction that has occurred calculated from 100 x the experimentally determined ratio of

Al(VI)/(Al(IV)+Al(V)) divided by the theoretical ratio It can be seen that at 1 day the percentage of the reaction increases with the Al:Si ratio of the glass. The reaction has gone 75% towards completion for the glass with an Al:Si ratio of 1 but only 43% towards completion for the lowest Al:Si ratio. On increasing the ageing time to 28 days the reaction has continued towards completion for all three cements.

4.0 Conclusions

The Al:Si ratio of the glass determines the reactivity of the glass and the resulting cement properties, including setting and working times and compressive strength. High Al:Si ratios above 0.8 result in very reactive glasses that are too reactive and have working that are too short for practical applications.

Glasses with Al:Si ratios below 0.5 exhibit poor compressive strengths. Glasses with Al:Si ratios between 0.5 and 0.8 are most appropriate for forming glass polyalkenoate cements.

The cement forming reaction can be followed by FTIR spectroscopy by measuring the absorbance ratios at 1550 and 1700cm^{-1} and by measuring the ratios of Al(VI)/(Al(IV)+Al(V)) using ^{27}Al MAS-NMR.

The proportion of free carboxyl group to carboxylate group reduces with time and the ratio of Al(VI)/(Al(IV)+Al(V))in the cement also increases with time. The increase in the compressive strength is consistent with increased ionic cross-linking of carboxylic acid groups with time.

5.0 References

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Table 1 Compositions of the glasses their Al:Si ratios

	X	SiO_2	$A_{l2}O_3$	CaO	Al:Si
HTM0		50	25	25	1.00
HTM1		56	22	22	0.79
HTM2		60	20	20	0.67
HTM3		64	18	18	0.56
HTM4		68	16	16	0.47
HTM5		72	14	14	0.39

Table 2 Particle Size Analysis of the Glasses

Glass	Al:Si	D (0.9)	D(0.5)	D(0.1)
HTM0	1.00	25.36	5.77	0.82
HTM1	0.79	19.34	3.66	0.76
HTM2	0.67	26.55	5.78	0.88
HTM3	0.56	30.58	7.47	1.07
HTM4	0.47	28.99	7.13	1.03
HTM5	0.39	?	?	?

Table 3 Data from Integrated Peak Areas of ^{27}Al MAS-NMR Spectra

HMT0	Al(IV)+Al(V)	Al(VI)	Al(VI)/(Al(IV)+A(V))	0.262 % Conversion
1 day	1	0.197	0.197	75%
28 days	0.900	0.190	0.212	81%
HMT2	Al(IV)+Al(V)	Al(VI)	Al(VI)/(Al(IV)+A(V))	0.336
1 day	0.832	0.179	0.215	64%
28 days	0.616	0.209	0.339	100%
HMT5	Al(IV)+Al(V)	Al(VI)	Al(VI)/(Al(IV)+A(V))	0.525
1 day	0.558	0.105	0.189	36
28 days	0.475	0.121	0.255	49

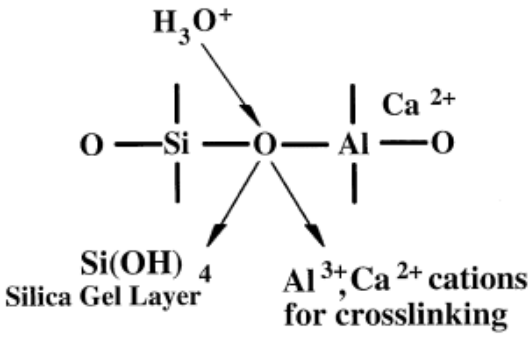

Figure 1 Acid Hydrolysis of Al-O-Si Bonds on the Glass Network

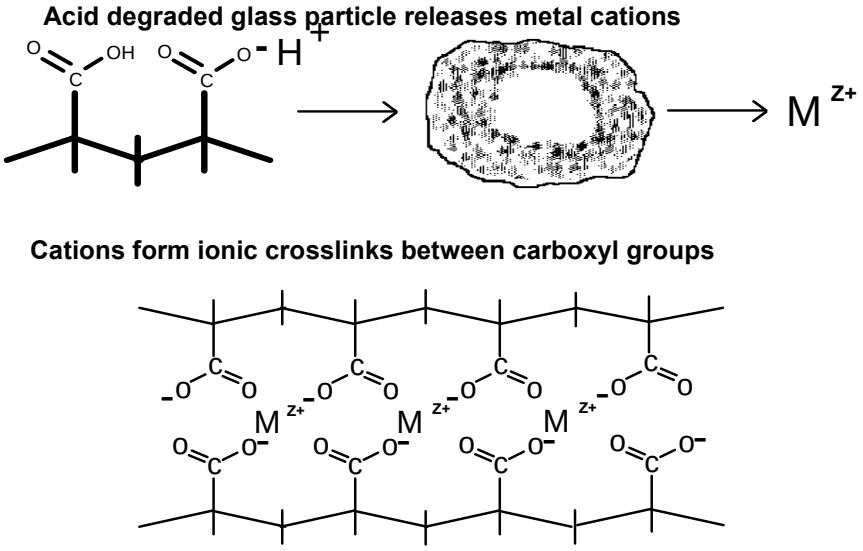

Figure 1 Schematic of the Setting Reaction.

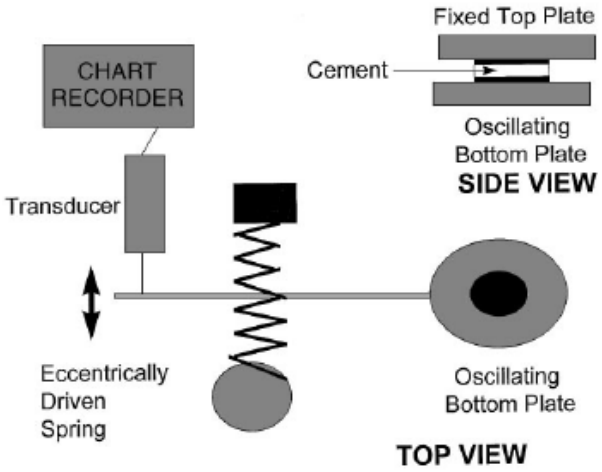

Figure 2a Schematic diagram of an oscillating rheometer. Working time was taken as corresponding to 95% de#ection and setting time as 5% of deflection.

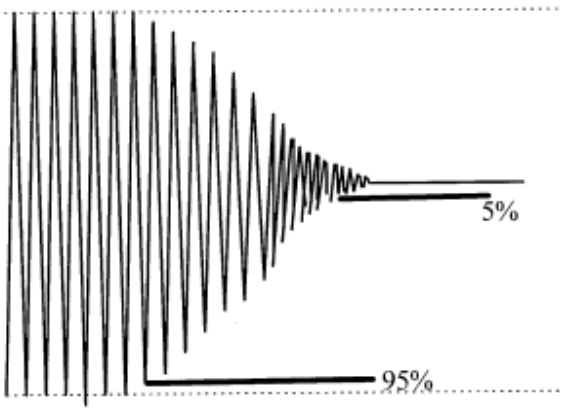

Figure 2b Typical Oscillating Rheometer Trace For a Setting Cement.

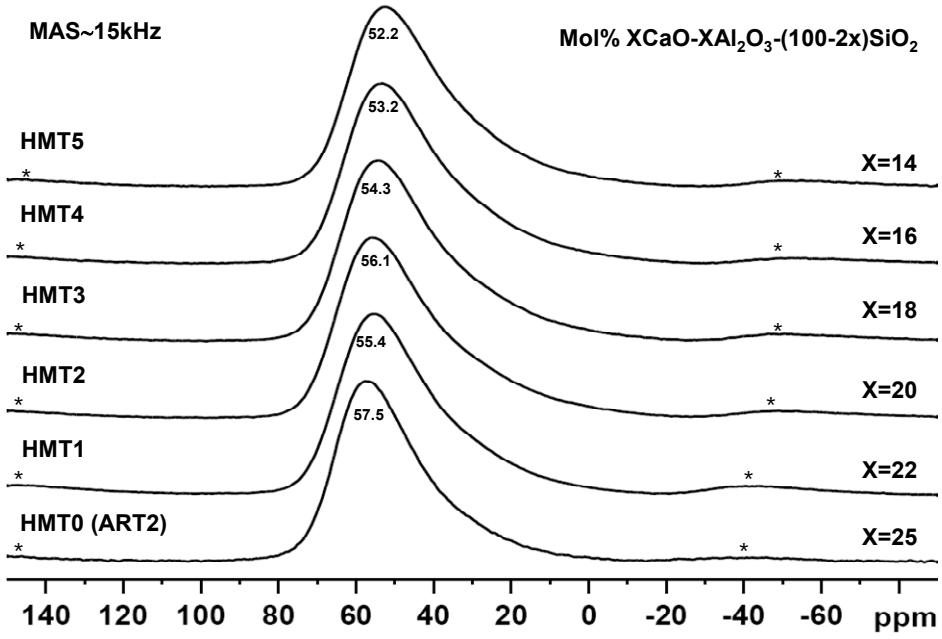

Figure 3 ^{27}Al MAS-NMR Specta One Out?

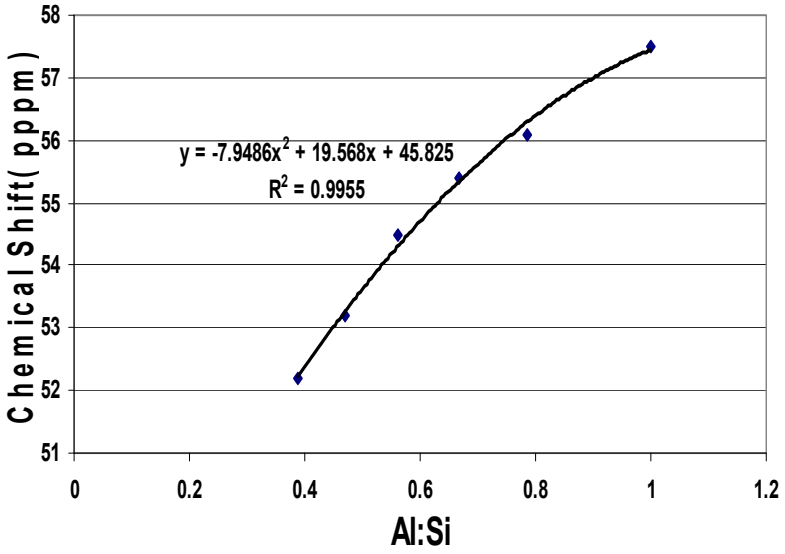

Figure 4 ^{27}Al Chemical Shift Plotted Against Al:Si ratio.

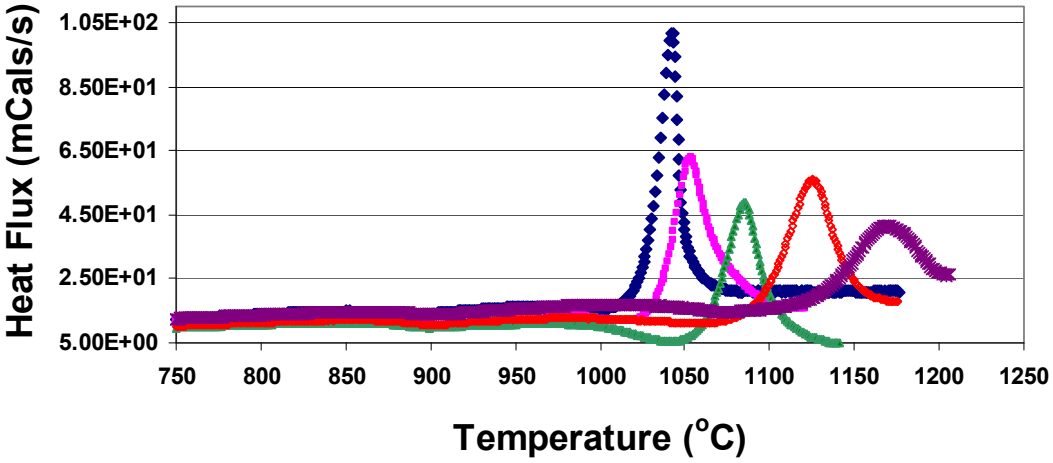

Figure 5 DSC Traces of the Glasses HTM1 to HTM5

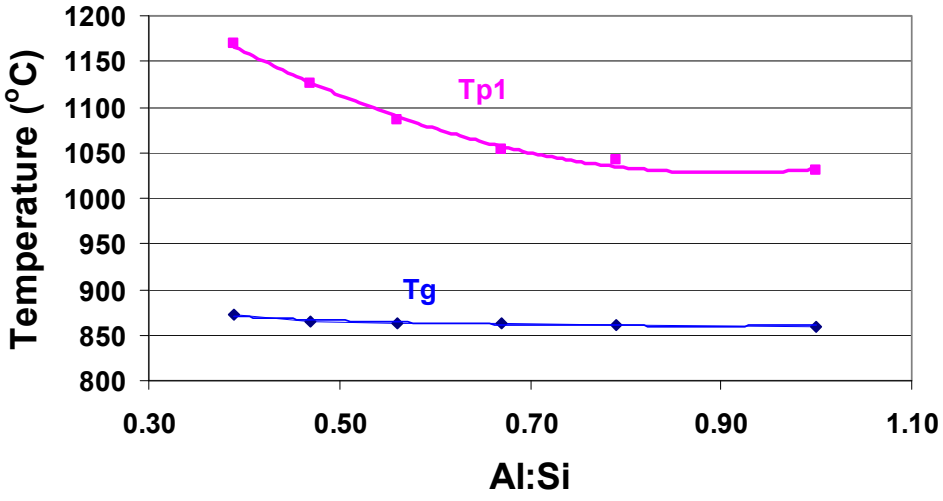

Figure 6 Tg and the Peak Crystallisation Temperature Plotted Against Al:Si Ratio.

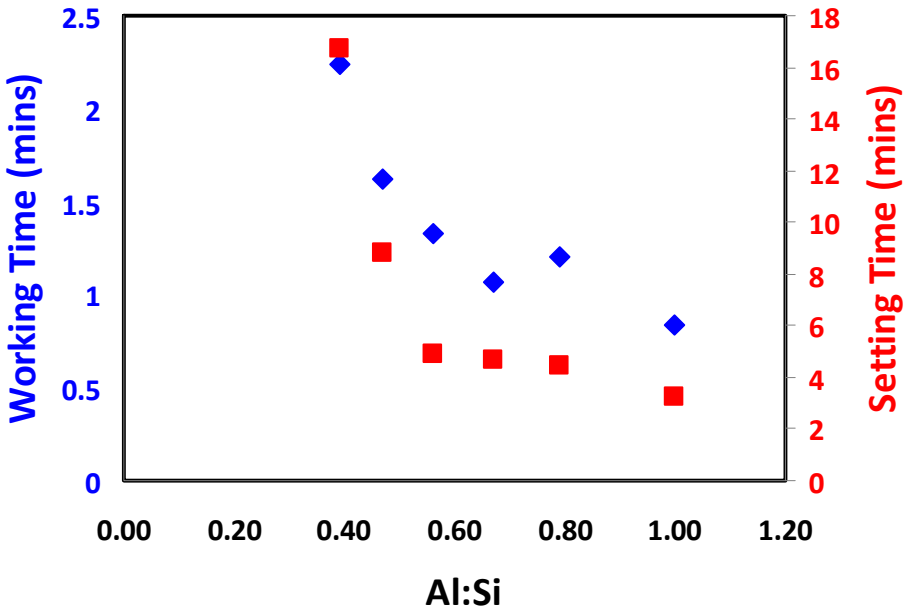

Figure 7 Working and Setting Times of the Cement Pastes Plotted Against Al:Si

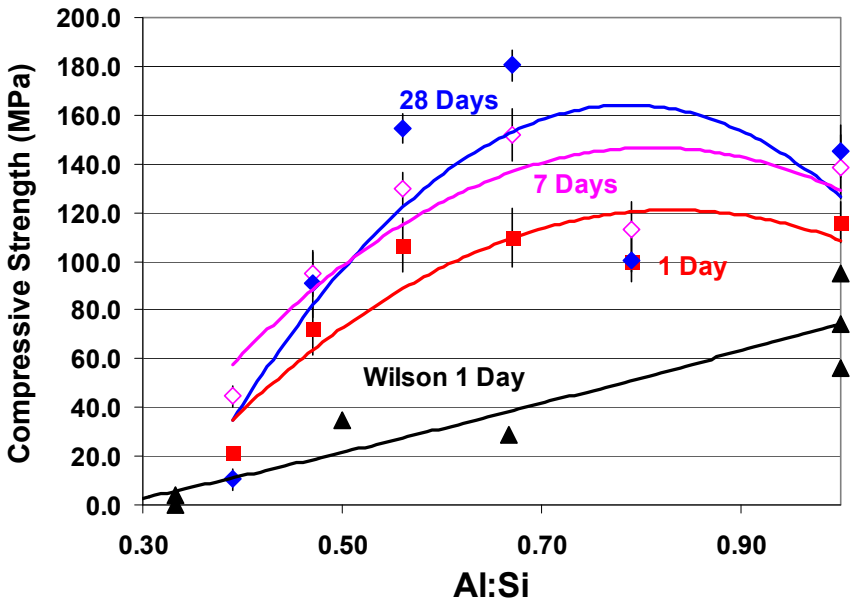

Figure 8 Compressive Strength Plotted Against the Al:Si Ratio
The triangles are the data from Wilson *et al.*[16]

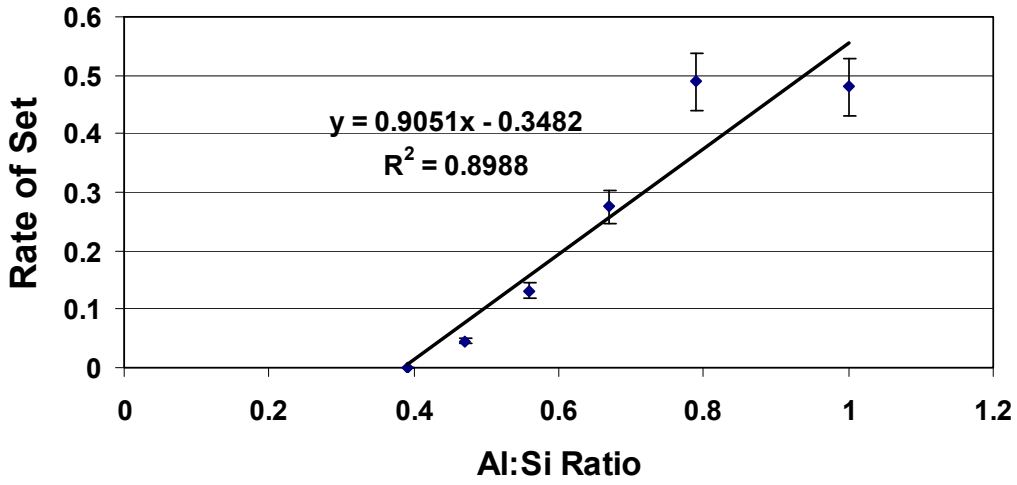

Figure 9 Rate of Set obtained from the Slopes of the Absorbance Ratio at 1550cm^{-1}/1700cm^{-1} over the first hour of setting plotted against the Al:Si ratio

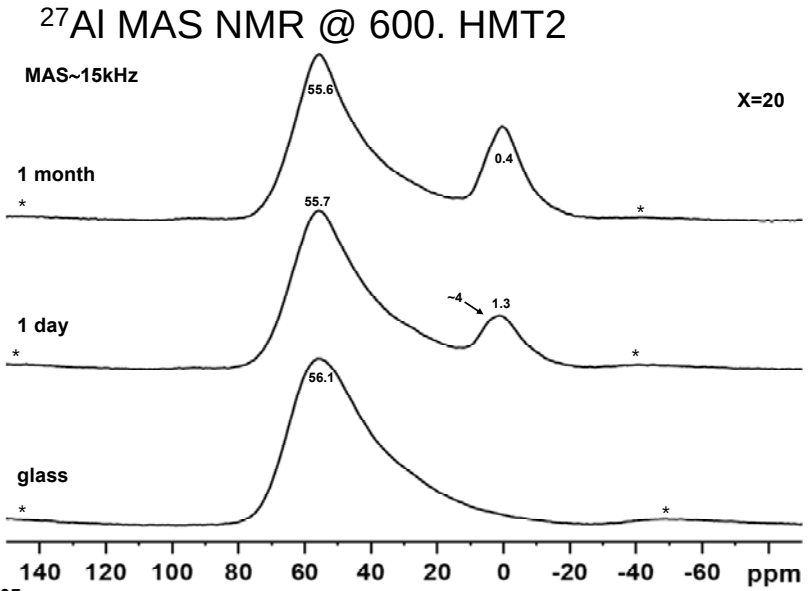

Figure 10 ^{27}Al Spectra for HTM2 (X=20) Glass and 1 Day and 28 Day Cements.

APPENDIX B

ABSTRACTS FOR PRESENTATIONS

Fluoride Release from Fluoroaluminosilicate Glasses in Water and Artificial Saliva *

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Objectives: Most studies related to fluoride release from glass ionomer cements have used deionised water as an elution media which does not represent the complex oral environment. This study used artificial saliva (AS) (Fusayama et al. 1963), to compare fluoride release from four experimental fluoroaluminosilicate glasses (AH2, LG26Sr, LG125 and LG26) in deionised water and artificial saliva. All the glasses contained Al, F, P, O and Si. The LG glasses were identical except the Ca in LG26 which was partially replaced by Sr in LG125 and totally in LG26Sr. AH2 was totally differently formulated containing Na and 2.5 times more fluoride than LG glasses.

Methods: The glasses were used as untreated glass, after acid-washing, and as a hydrolytically unstable pseudocement with acetic acid. For each type six samples were evaluated after immersion in deionised water and artificial saliva respectively. The samples were centrifuged and the immersing solutions collected and changed at 1,3,7,14,21 and 28 days. The collected solutions were tested for free and complex fluoride using ion selective electrode. Cumulative fluoride release against square root of time was plotted. Statistical analysis was performed using t-test

Results: On immersion in AS, AH2 glass showed a significantly greater fluoride release than in water ($p = or < 0.002$) with a 75% mean increase. This is in contrast to the LG glasses where the fluoride release was significantly reduced ($p = or < 0.005$) with a mean reduction of 52%. Under all conditions AH2 always released substantially more fluoride than LG glasses.

Conclusion: Fluoride release in deionised water does not represent the fluoride release in the oral environment, however in both media it was diffusion controlled mechanism. Furthermore, it was also concluded that the fluoride release from FAS is higher than cements and is influenced by glass composition.

* *PEF IADR 2006*

Effect of Ultrasound on Zinc Polycarboxylate Cements *

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The set of glass ionomer cement (GIC) is accelerated by application of ultrasound. Although GIC has somewhat displaced zinc polycarboxylate cement (ZPC) in dental applications the latter is still extensively used. Like GIC, it provides direct adhesion to tooth and can provide F release, but is more radiopaque and biocompatible than GIC.

Objectives: The aim of this study is to examine the effect of ultrasound on the setting of ZPC using Fourier Transform Infra Red spectroscopy and any interaction with SnF_2 addition.

Methods: ZPC with and without SnF_2 addition(+/-S) at luting (L) 2:1 P/L ratio and restorative (R) 4:1 P/L ratio consistencies. Ultrasound is applied to the cement using Piezon-Master 400, EMS, Switzerland at 60s from start of mixing for 15s.

Results: The ratios of absorbance peak height at $1400cm^{-1}$ $-COO^-$ to that at $1630cm^{-1}$ –COOH were measured and compared those obtained for the cement not treated with US. These values were taken at the elapsed time at which no further change in spectrum [ratio] was observed at room temperature [10 to 20 min]. The US results are taken at 2 or3 minutes.

	R/+S	**R/-S**	**L/+S**	**L/-S**
No US	1.09	1.2	1.07	1.04
US	1.50	1.64	1.38	1.05

The results show all four ZPC formulations are very sensitive to ultrasound whether with or without SnF_2. Reducing US to 10s produces lower initial ratios but these increase up to 10min when very high ratios (>2) are obtained. Previous studies with restorative GICs found that 40-55s US was needed to produce the effect found with 15s on ZPCs. ZPC powder is more basic than GIC glass ; this may account for ZPC's greater sensitivity to US.

Conclusions: Ultrasound may provide a useful adjunct to the clinical use of ZPC both as luting agent and temporary restorative.

**PEF IADR 2006*

Investigation into Secondary Setting Mechanism of Glass-Ionomers*

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Queen Mary University of London, United Kingdom

Objectives: From the development of hydrolytic stability by cements formed by glass ionomer cement (GIC) glass and acetic acid Wasson and Nicholson deduced that a "silica phase" was the mechanism responsible for the maturation of GIC. However, only one glass, G338, was investigated. Previously, we repeated their work using MP4 a glass without F and P. This did not produce hydrolytically stable cement with acetic acid although containing more silica than G338. This suggests that factors other than silica control the secondary setting mechanism. The current study evaluates whether the anion-forming elements F and P are responsible for the hydrolytic stability of glass/acetic acid cements.

Materials and Methods: Aluminosilicates glasses LG30, LG117 and LG26 were used. LG26 contained both F and P, LG117 F only, and LG30 P only. Al, Si and Ca contents were the same. The glasses were mixed with 45% acetic acid at a P/L ratio of 4/1 and made into discs 1mm x 10mm. These were matured at 37^{o}C for 1, 2, 3, 6 and 24 hours then dropped into 40ml of deionised water. After 24hours they were assessed for visual disintegration using a scale developed for this purpose. A score of 1/5 (0.2) indicated a highly stable cement whereas 5/5 (1.0) complete disintegration.

Results: See Table 1. Hydrolytically stable cements were formed with LG30 after 24hours whereas with LG117 and LG26 they were after only 1 hour and all subsequent times.

Table 1: Hydrolytic stability according to the point score system.

	1hr	2hr	3hr	6hr	24hr	Total points
LG30	0.8	0.8	0.8	0.8	0.2	3.4
LG26	0.2	0.2	0.2	0.2	0.2	1
LG117	0.2	0.2	0.2	0.2	0.2	1

Conclusions: Precipitation of insoluble Ca salts, particularly calcium fluoride, appears a likely explanation of cement stability.

**BSDR NOF 2007*

Effect of sodium monofluorophosphate on glass ionomer surfaces*

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[2]Imperial College, London, United Kingdom

The ability of glass ionomer cements (GICs) to take up therapeutic ions, e.g. K^+ and F^-, is widely reported. F^-ions also disrupt the GIC surface. Monofluorophosphate (MFP) ion is a therapeutic alternative to F^-. **Objectives:** This study is designed to examine the effect of MFP on GIC surfaces and the effect of its addition to an F-free GIC.

Methods: Two GICs were used with different glasses but otherwise identical compositions. AH2 contained F, LG30 was essentially F-free. 3% NaMFP solution was used for immersion and 0.2% NaF for comparison. Discs were made from the cements and matured at 37ºC and >95%r.h. for 24hours. Immersion was for 24hours in water, or NaMFP, or NaF. Surfaces were examined with an SEM. In addition, LG30 was formulated with 4.3% NaMFP added (LG30+MFP). This was treated as above and the cement discs had their roughness (Ra) measured using a Mitutoya Surftest.

Results: The AH2 surfaces exposed to NaMFP were considerably disrupted (compared to water exposed one) though less than those exposed to NaF. Very slight disruption was observed for LG30/MFP and LG30/NaF. For LG30+MFP the Ra values (μm, n=10) after immersion were MFP 3.97(0.65); NaF 2.99(1.28); H_2O 0.55(0.25). Statistical analysis (Wilcoxon) showed both NaF and MFP to be significantly ($p<0.05$) rougher than H_2O but not significantly different to each other.

Discussion: When exposed to MFP GICs behave very similarly when exposed to F^-. When MFP was added to a GIC without F it rendered it susceptible to surface disruption as previous studies showed NaF addition did. Possibly MFP may be hydrolysed to F in the initial low pH conditions of the mixed GIC.

Conclusion: MFP behaves similarly to NaF both when added to an F-free GIC and when an F-containing GIC is immersed in its solution for a prolonged period.

**BSDR NOF 2007*

Investigation of F-release from glass-ionomer cement by ultrasound *

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Queen Mary University of London, United Kingdom

Ultrasound has been shown to enhance the fluoride release of conventional glass ionomer cements (GICs). However it the mechanism of this effect is not clear.

Objectives: The aim of this study is to differentiate between greater reaction releasing more F from glass into matrix and changes in cement resulting in higher F diffusion.

Methods: Experimental GIC glass LG30 having only impurity level of F was formulated as water-mix GIC. It was mixed with either water (W) or 2% NaF (N) at a powder liquid ratio of 7:1. 2 x 2mm samples were made in cylindrical moulds .Samples (n=5) were either set with ultrasound for 55 seconds (U) or allowed to self-cure at room temperature (SC). The samples were de-moulded and placed in 10ml of deionsed water in an oven at 37 ^{o}C. The water was changed during intervals of 1,3,7,14,21 & 28 days. Aliquots were taken and measured with an Ion selective electrode for free fluoride in deionised water and total fluoride measured by buffering with TISAB IV.

Results: The results showed that US set LG30 + NaF released 1.28 times more fluoride compared to SC set LG30 + NaF. However the LG30 cummulative fluoride release was ~ 3times than SC LG30. The cumulative fluoride release was linear to $t^{1/2}$. The initial burst of fluoride (C=-intercept) and the total fluoride release (m=gradient) is as follows:

	NU	**N SC**	**WU**	**WSC**
m	0.0046	0.0036	0.0009	0.0003
C	0.0041	0.0035	0.0002	0.0004

Compared to a previous study the amount of fluoride released from N was very small because of the amount of fluoride present in the cement. The effect of ultrasound was very slight compared to cements with F in the glass.

Conclusion: Ultrasound has a direct effect on the GIC reaction rather than on the diffusion of F through the cement.

* *BSDR NOF 2007*

Influence of Ultrasound on Glass Ionomer/Fluoride Interaction*

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Queen Mary University of London, United Kingdom

Glass ionomer cements (GICs) are influenced by ultrasound application which results in increased strength and also increased fluoride release. GICs also take up F^- from alkali metal fluoride solution

Objectives: This study aims to evaluate the effect of ultrasound on F- uptake by GICs

Methods: Encapsulated GIC Amalgomer (Am) and Fuji IX (Fu) were mixed according to manufacturer instructions and packed into 2mm x 3mm cylindrical moulds. Those setting normally (SC) were immediately transferred to an oven kept at 37C and 100% relative humidity for one hour. Ultrasonically cured samples (UC) were subjected to 55sec of US at exactly 1 min after mixing; thereafter these samples were also transferred to the oven for 1 hour. After 1 hour the samples were removed and 3 cylinders were dropped into each 4ml of 0.2% NaF solution. The sample size was n=6 for each group These were then kept in the incubator for 24 hours after which the immersing solutions were collected and checked for F^- concentration using an ion selective F^- electrode using TISAB IV as a decomplexing agent.. F^- uptake was calculated as (control solution – test solution).

Results: There was a significant difference in uptake between Am and Fu SC ($p=0.02$). US significantly reduced the uptake of F^- by both the materials ($p<0.05$). For Fu this reduction was 72% whereas for Am it was only 17%.

Conclusions: Ultrasound significantly reduces the uptake of F^- by GIC. The size of effect varies between two GICs studie

**PEF IADR 2008*

Effect of Ultrasound and Heat on F-Release from Glass Ionomer *

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Introduction: The application of ultrasound (US) to glass ionomer cement (gic) produces rapid set and enhanced mechanical properties. It additionally enhances the release of F^- ion. Glass Carbomer (GC) is an improved variant of gic produced by siloxane incorporation. The manufacturers advocate the application of heat produced by a curing light (LH) unit to produce the effects on set and mechanical properties obtained with US.

Objectives: This study aims to compare the effects of US and LH on the release of F^- ion.

Methods: GC capsules were mixed in a vibrator as per instructions. Cylindrical samples were produced 2 x 3mm high and cured either with US, LH or without either were self cured (SC). Samples [n=6] were stored in 10mL of deionized water which was changed at 1,3,7 14,21,& 28 days. F^-ion content was determined using an ion selective electrode. The F^- ion content of the batch of deionized water used was determined as blank.

Results: The mg F^-ion/g cement were plotted as cumulative values against $t^{½}$ and showed a linear relationship with R^2 0.993 or greater. The values of m and C for these equations are shown in table.

Material	m	C	R^2
GC/SC	0.129	0.064	0.998
GC/US	0.345	0.101	0.997
GC/LH	0.102	0.036	0.993

The effects of US and LH are in opposite directions (compared to SC) and are statistically significantly different p=0.05.

Discussion: The effect on release of LH (v.SC) is much less than US. Its cumulative result at 28 days is 0.75x SC whereas US is 2.6x. The effect of US on F^- release is similar to that found with several other gics.

Conclusions: Heat and ultrasound affect F release from a gic in opposite directions; so the effect of ultrasound on gic is not solely related to its heating effect.

** PEF IADR 2008*

Effect of Glass Composition On Hydrolytic Stability of Acetate Cements*

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[1]Queen Mary University of London, [2]Imperial College, London,

Objectives: Previously it was shown that a conventional glass ionomer cement (GIC) glass G338 formed a hydrolytically stable cement with acetic acid solution. When this glass was replaced with one without F or P the cement was not stable. This study was designed to use glasses with only F or P to elucidate the effect. In addition, since the F and P free glass was relatively high in Na, a similar Na-free glass was to be tested.

Methods: The glasses contain Al, Ca, Si, and O; other elements are given in the table. Glasses were mixed with 45% acetic acid at a P:L ratio of 4:1.The mix was packed into moulds 1 mm thick and 10 mm in diameter and allowed to set for 1, 2, 3, 6 and 24 h. They were then dropped into 40 mL of deionised water to assess hydrolytic stability. The assessment was performed by visual examination based on a points score system from 1 "fully intact" to 5 "total disintegration".

	F%	P%	Na
LG26	6.7	8.6	-
LG30	0.04	6.4	0.05
LG117	6.1	-	-
Anorthite	-	-	-
G338	19.7	6.2	6.3
MP4	-	-	8.2

Results: The results are given in the table below with those previously obtained for G338 and MP4. G338 is similar to LG26 and Anorthite to MP4 except for their Na contents.

	1hr	2hr	3hr	6hr	24hr	Total points
LG26	1	1	1	1	1	5
LG30	1	1	1	1	1	5
LG117	1	1	1	1	1	5
Anorthite	1	1	1	1	1	5
G338	4	4	1	1	1	11
MP4	5	5	5	5	5	25

Conclusions: The hydrolytic stability of glass acetate cements is influenced by Na content of the glass.

**BSDR 2009*